

Application No. 10/686,697
Paper Dated: March 30, 2009
In Reply to USPTO Correspondence of October 3, 2008
Attorney Docket No. 5219-061243

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Application No. : 10/686,697 Confirmation No. 7668
Applicant : PAUL A. KOHL
Filed : October 16, 2003
Title : POLYMERS, METHODS OF USE THEREOF, AND
METHODS OF DECOMPOSITION THEREOF
Group Art Unit : 1795
Examiner : Sin J. Lee
Customer No. : 28289

Mail Stop Amendment
Commissioner for Patents
P. O. Box 1450
Alexandria, VA 22313-1450

DECLARATION UNDER 37 CFR § 1.131
SHOWING CONCEPTION AND DILIGENCE
PRIOR TO SEPTEMBER 13, 2002 UNTIL FILING

Sir:

I, Paul A. Kohl, hereby declare as follows:

1. I along with SueAnn Bidstrup Allen, Xiaoqun Wu and Clifford Lee Henderson are the named inventors and assignees of the invention described and claimed in the above-captioned application. A copy of my curriculum vitae is included as Exhibit A.

2. As evidenced by the attached Exhibit B, the present invention was first conceived on July 24, 2000 (page 3) and later disclosed in an Invention Disclosure Form (IDF) provided by the Georgia Tech Research Corporation Office of Technology Transfer, which is dated February 12, 2001 (page 1). The Invention Disclosure Form was signed by two witnesses on February 7, 2001 (page 4). Please note that references to page numbering of Exhibit B correspond to the number located at the bottom right hand corner of each page.

3. The IDF and accompanying figures are directed to a method of fabricating microchannels using polynorbornene photosensitive sacrificial materials. The materials describe the fabrication of the microchannels by the thermal decomposition of the sacrificial polymers, thus forming air channels. See pages 6, 19-20; Figure 1. The IDF describes the composition of the sacrificial polymer including the thermal decomposition characteristics (page 13; Figures 6 and 7); microchannel fabrication (pages 13-14) and the calculation of the thermal decomposition profile (pages 13-16). The results clearly describe the successful fabrication of microchannels. See pages 16-26; Figures 11-13.

4. From July 24, 2000 until February 12, 2001, we proceeded diligently to work on the development of the sacrificial polymer fabrication methods to produce channel geometries with arbitrary shaped cross-sectional profiles by developing channel geometries, synthesizing various sacrificial polymers, determining thermal decomposition characteristics and fabricating microchannels.

5. The present application claims the benefit of U.S. Provisional Patent Application No. 60/418,930, dated October 16, 2002, which is the effective filing date of the present application.

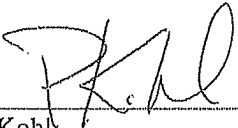
6. From February 12, 2001 until the United States effective filing date of October 16, 2002, the inventors prepared and finalized the figures, explained the invention to patent counsel and reviewed the patent application prepared by patent counsel.

7. The above utility application was subsequently filed in the United States Patent and Trademark Office on October 16, 2003, claiming the benefit of the corresponding U.S. Provisional Patent Application.

8. The aforementioned activities, from about July 2000 to August 2002 (Exhibit B), demonstrate the required evidence of conception prior to the effective date of the cited reference, i.e., September 13, 2002, as well as diligence and constructive reduction to practice of the present invention.

Application No. 10/686,697
Paper Dated: March 30, 2009
In Reply to USPTO Correspondence of October 3, 2008
Attorney Docket No. 5219-061243

9. I declare further that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true, and further that these statements are made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.



Paul A. Kohl

3/30/2009
Date

Paul A. Kohl
Regents' Professor
School of Chemical and Biomolecular Engineering

EARNED DEGREES

<u>Degree</u>	<u>Year</u>	<u>University</u>	<u>Field</u>
Ph.D.	1978	University of Texas at Austin	Chemistry
B.S.	1974	Bethany College	Chemistry

EMPLOYMENT

<u>Title</u>	<u>Organization</u>	<u>Years</u>
Director, SRC Interconnect and Packaging Center at Georgia Tech		2009-present
Hercules Inc./Thomas L. Gossage Chair	Georgia Tech	2006-present
Director, Interconnect Focus Center	MARCO Center homed at GT	2006-present
Regents' Professor	Georgia Tech	1999-present
Institute Fellow	Georgia Tech	1996
Professor	Georgia Tech	1994-1999
Associate Professor	Georgia Tech	1989-1994
Technical Supervisor	AT&T Bell Laboratories	1982-1989J
Member of Technical Staff	AT&T Bell Laboratories	1978-1982

HONORS AND AWARDS

1. Analytical Chemistry Award from the American Chemical Society in 1973.
2. Awarded Academic Distinction in chemistry from Bethany College in 1974.
3. Gilbert H. Ayers for outstanding graduate work in chemistry in 1977.
4. Edward Weston Fellowship from the Electrochemical Society in 1977.
5. Named one of "America's 100 Brightest Scientists Under 40" by Science Digest in 1985.
6. Outstanding Alumni Achievement Award presented by Bethany College in 1986.
7. Outstanding Faculty Award, 1990-1991, AIChE Student Chapter Georgia Tech.
8. Outstanding Faculty Award, 1990-1991, Chemical Engineering, Georgia Tech.
9. Named Institute Fellow, 1994, Georgia Tech.
10. Research Program Development Award, 1995, Georgia Tech.

11. Research Award: NSF-ERC in Electronic Packaging, 1999.
12. Zeigler Outstanding Faculty, 2000-2001, School of Chemical Engineering, Georgia Tech.
13. Carl Wagner Memorial Award, The Electrochemical Society, 2001.
14. Named Fellow of The Electrochemical Society, October 2002.
15. Best Paper Award, IEEE 52nd Electronic Components and Technology Conference, 2002.
16. Thomas D. Callinan Award, Electrochemical Society, 2008.

SCHOLARLY ACCOMPLISHMENTS

A. Published Books and Parts of Books

Hodge, T.C., Kohl, P.A., Bidstrup, S.A., Lee, J.B., and Allen M.A., "In-situ thermal Expansion Measurements of Interlevel Dielectric Polymer Films", *Polyimides: Trends in Materials & Applications*, (C. Feger, M. Khojastan, S. Molis Eds.) 287-302, Society of Plastic Engineers.

Kohl, P. A., "Electrodeposition of Gold", in *Modern Electroplating*, (M. Schlesinger, M. Paniov, Eds) Wiley and Sons, 2000.

Faulkner, L. R., Bullock, K. R., Kohl, P. A., Kukkonen, C. A., MacLachlan, A., McIntyre, J. A., Miller, B., Morrison, D. L., Vyas, B., and Weaver, R. D., "Effectiveness of the United States Advanced Battery Consortium as a government-Industry Partnership", National Research Council, 1998.

Kohl, P. A., "Air-Gaps for Electrical Interconnections", in *Encyclopedia of Materials: Science and Technology* (H. L. Gossmann Ed), Pergamon, 2000.

Kohl, P.A., Chapter 8: "Chip-to-Module Interconnection" in "Interconnect Technology and Design for Gigascale Integration", J. Davis, and J. D. Meindl, Ed., 2003.

Meindl, J. D., Davis, J., Zarkesh-Ha, P., Patel, C., Martin, K. P., and Kohl, P.A., Chapter 1: "Interconnect Opportunities for GSI" in "Interconnect Technology and Design for Gigascale Integration", J. Davis, and J. D. Meindl, Ed., 2003.

Kohl, P. A., Chapter on "Compliant Interconnects" in "New Trends in Electrochemical Technology", Eds: M. Datta, T. Osaka, and J. W. Schultze, 2004.

Kohl, P. A., Osborn, T., and He, A., Chapter on "Advanced Chip-to-Substrate

Connections", in *Materials for Advanced Packaging*, Eds. Wong and Lu, Wiley, 2008.

Prakash, S., Mustain, W., and Kohl P. A., "Electrolytes for Long-Life, Ultra Low-Power Direct Methanol Fuel Cells" in *Advances in Fuel Cells*, Elsevier, 2008.

B. Published Refereed Journal Papers

1. Kohl, P.A., and Bard, A.J., "The Characterization and Behavior of n-Type ZnO, CdS and GaP Electrodes in Acetonitrile Solutions", Journal of the American Chemical Society, 99, 7531-7539 (1977).
2. Kohl, P.A., Frank, S.N., and Bard, A.J., "Behavior of n- and p-Type single Crystal Semiconductors Covered with Thin n-TiO₂ Films", Journal of the Electrochemical Society, 124, 225-229 (1977).
3. Noufi, R.N., Kohl, P.A. and Bard, A.J., "Electrochemistry and Electroluminescence at n-Type TiO₂ in Aqueous Solutions", Journal of the Electrochemical Society, 125, 246-252 (1978).
4. Noufi, R.N., Kohl, P.A. and Bard, A.J., "Photoelectrochemical Cells with Mixed Polycrystalline n-Type CdS-CdSe Electrodes", Journal of the Electrochemical Society, 125 375-379 (1978).
5. Kohl, P.A. "The Electrochemical Behavior of n- and p-GaAs and InP in Nonaqueous Solutions", Journal of the Electrochemical Society, 125, 283-286 (1978).
6. Kohl, P.A. and Bard, A.J., "The Characterization and Behavior of n- and p-GaAs Electrodes in Acetonitrile Solutions", Journal of the Electrochemical Society, 126, 59-63 (1979).
7. Kohl, P.A., and Bard, A.J. "The Photoelectrochemical Behavior of n- and p-InP Electrodes in Acetonitrile Solutions", Journal of the Electrochemical Society, 126, 598-602 (1979).
8. Kohl, P.A., and Bard, A.J., "Liquid Junction Photovoltaic Cells Based on n-GaAs Electrodes in Acetonitrile Solutions", Journal of the Electrochemical Society, 126, 603-608 (1979).
9. Noufi, R.N., Kohl, P.A., Rogers, J.W., White, J.M., and Bard, A.J., "An Investigation of S/Se Substitution in single Crystal CdSe and CdS Photoelectrodes by Electron Spectroscopy", Journal of the Electrochemical Society, 126, 949-954 (1979).
10. Ostermayer, F.W. Jr. and Kohl, P.A., "Photoelectrochemical Etching of p-GaAs", Applied Physics Letters, 39, 76-78 (1981).

11. Kohl, P.A., "High Speed Solder Plating Baths", Plating and Surface Finishing, 45-48 (1981).
12. Kohl, P.A., Wolowodiuk, and Ostermayer, F.W., Jr., "The Photoelectrochemical Oxidation of (100), (111) and (111) n-InP and n-GaAs", Journal of the Electrochemical Society, 130, 2288-2293 (1983).
13. Kohl, P.A., "The High Speed Electrodeposition of Sn/Pb Alloys", Journal of the Electrochemical Society, 129, 1196-1199 (1982).
14. Kohl, P.A., "Hochgeschwindigkeitsabscheidung von Sn-Blei-Legierungen". Oberfläche Surface, 23 (b), 190-194 (1982).
15. Forrest, S.R., Kohl, P.A., Panock, R., DeWinter, J.W., Nahory, R.E., and Yanowski, E., "A Long-wavelength, Annular In_{0.53}Ga_{0.47}As, p-i-n Photodector", IEEE Electron Device Letters, EDL-3, 415-417 (1982).
16. Ostermayer, F.W., Kohl, P.A., and Burton, R.H., "Photoelectrochemical Etching of Integral Lenses on InP/InGaAsP LEDs", Applied Physics Letters, 43, 642-644 (1983).
17. Ostermayer, F.W., Kohl, P.A., and Lum, R.M., "Hole Transport Equation Analysis of Photoelectrochemical Etching Resolution", Journal of Applied Physics, 58, 4390-4395 (1985).
18. Kohl, P.A., D'Asaro, L.A., Wolowodiuk, C. and Ostermayer, Jr., F.W., "Photoelectrochemical Plating of GaAs FETs", Electron Device Letters, EDL-5, 7-9 (1984).
19. Panock, R., Forrest, S.R., Kohl, P.A., deWinter, J.C., Nahary, R.E., and Yanowski, E.D, "An Experimental Low-loss Single-wavelength Bidirectional Lightwave Link", Journal of Lightwave Technology, LT2 (3), 300-304 (1984).
20. Kohl, P.A., Ballman, A.A., and Logan, R.A., "Holographic Photoelectrochemical Etching of Diffusion Gratings in n-InP and n-GaAsP for Distributed Feedback Lasers", Journal of Applied Physics, 57, 39-43 (1985).
21. Lum, R.M., Ostermayer, F.W., Kohl, P.A., Glass, A.M., and Ballman, A.A., "Improvements in the Modulation Amplitude of Submicron Gratings Produced in n-InP by Direct Photoelectrochemical Etching", Applied Physics Letters, 47, 269-271 (1985).
22. Kohl, P.A. and Ostermayer, F.W., Jr., "Photoelectrochemical Methods for III-V Semiconductor Device Processing", Annual Review of Material Science, 19, 379-399 (1989).

23. Kohl, P.A., Harris, D.B., and Winnick, J., "P-InP Photoetching", Journal of the Electrochemical Society, 137, 3315-3316 (1990).
24. Kohl, P.A., Harris, D.B., and Winnick, J., "The Photoelectrochemical Etching of (100) and (111) p-InP", Journal of the Electrochemical Society, 138, 608-611 (1991).
25. Yu, C.L., Winnick, J., and Kohl, P.A., "A Novel Electrolyte for Na/Fe Cl₂ Battery", Journal of the Electrochemical Society, 138, 339-340 (1991).
26. Kohl, P.A., and Harris, D.B., "Photoelectrochemical Methods for Semiconductor Device Processing", Electrochimica Acta, 38, 101-106 (1993).
27. Twyford, E.J., Kohl, P.A., Jokerst, N.M., and Hartman, N.F., "The Formation of Submicron Gratings", Applied Physics Letters, 60, 2528-30 (1992).
28. Kowalik, J., Tolbert, L.M., Ding, Y., Bottomley, L.A., Vogt, K., and Kohl, P.A., "The Characterization of Strongly Adherent and Self Doped Electrically Conductive Polymer Films", Synthetic Metals, 55, 1171-5 (1993).
29. Propst, E., and Kohl, P.A., "The Photoelectrochemical Oxidation of n-Si in Anhydrous HF-Acetonitrile", Journal of the Electrochemical Society, 140, L78-80 (1993).
30. Harris, D.B., Winnick, J., and Kohl, P.A., "Cation Effect on the CdSe liquid Junction", Journal of the Electrochemical Society, 140, 2581-2588 (1993).
31. Vogt, K., Kohl, P.A., Bell, R., Bottomley, L.A., and Carter, B., "Characterization of Thin Titanium Oxide Adhesion Layers on Gold: Resistivity, Morphology, and Composition.", Surface Science, 301, 203-213 (1994).
32. Propst, E., Vogt, K., and Kohl, P.A., "The Photoelectrochemical Etching of GaSb", Journal of the Electrochemical Society, 140, 3631-5 (1993).
33. Cloud, T., Houston, M., Kohl, P.A., and Bidstrup, S.A., "High Performance Noble Metal MCMs" IEEE CHMT, 16, 724-730 (1993).
34. Vogt, K., and Kohl, P.A., "GaAs Passivation Through Nitridation with Hydrazine", Journal of Applied Physics, 74, 6448 (1993).
35. Hodge, T.C., Landmann, B., Kohl, P.A., and Bidstrup, S.A., "Rapid Thermal Curing of Polymer Interlayer Dielectrics" International Journal of Microcircuits & Electronic Packaging, 17, 10-20 (1994).
36. Propst, E., Rieger, M., and Kohl, P.A., "Luminescence and its Quenching From Porous Silicon Formed in a Non-aqueous Electrolyte" Applied Physics Letters, 64, 1914-16 (1994).

37. Propst, E., and Kohl, P.A., "The Electrochemical Oxidation of Silicon and Formation of Porous Silicon", Journal of the Electrochemical Society, **141**, 1006-1013 (1994).
38. Harris, D.B., Kohl, P.A., and Winnick, J., "Photoelectrochemical Processing of InAs", Journal of the Electrochemical Society, **141**, 1274-7 (1994).
39. S. Han, M. Ceiler, S. Bidstrup, P. Kohl, and G. May, "Modeling the Properties of PECVD Silicon Dioxide Films Using Optimized Back-Propagation Neural Networks," IEEE Transactions on Components, Hybrids, and Manufacturing Technology, **17**, 174-82 (1994).
40. Vogt, K.W., Naugher, L.A., and Kohl, P.A., "Low Temperature Nitridation of Transition Metals with Hydrazine", Thin Solid Films, **256**, 106-15 (1995).
41. Vogt, K.W., and Kohl, P.A., "Adhesion Layer Bonding of Light Weight Metals in Electronic Applications", Materials Technology, **9**, 145-7 (1995).
42. Vogt, K.W., Houston, M., Ceiler, M.F., Roberts, C.E., and Kohl, P.A., "Improvement in Dielectric Properties of Low Temperature PECVD Silicon Dioxide by Reaction with Hydrazine" Journal of Electronic Materials, **24**, 751-5 (1995).
43. Vogt, K.W., and P.A. Kohl, "Nitridation and CVD Reactions with Hydrazine", AIChE Journal, **41**, 2282-2291 (1995).
44. Rieger, M.M., and Kohl, P.A., "Mechanism of (111) Silicon Etching in HF-Acetonitrile", Journal of the Electrochemical Society, **142**, 1490-5 (1995).
45. Sullivan, A., and Kohl, P.A., "Electroless Deposition of Gold From a Non-Cyanide, Gold Thiosulfate Bath", Journal of the Electrochemical Society, **142**, 2272 (1995).
46. Ceiler, M., Kohl, P.A., and Bidstrup, S.A., "PECVD Silicon Dioxide Deposited at Low Temperatures", Journal of the Electrochemical Society, **142**, 2067-71 (1995).
47. Twyford, E.T., Jokerst, N.M., Kohl, P.A., and Tayag, J., "A Pixellated Grating Array Using Photoelectrochemical Etching on a GaAs Waveguide", IEEE Photonics Letters, **7**, 766-8 (1995).
48. Twyford, E.J., Carter, C.A., Kohl, P.A., and Jokerst, N.M., "The Influence of Aluminum Concentration on Photoelectrochemical Etching of First Order Gratings in GaAs/AlGaAs", Applied Physics Letters, **67**, 1182-1184 (1995).
49. Gray, G., Kohl, P.A., and Winnick, J., "Stability of Sodium Electrodeposited

from a Room Temperature Chloroaluminate Molten Salt", Journal of the Electrochemical Society, 142, 3636-3642 (1995).

50. Gray, G., and Winnick, J., and Kohl, P.A., "Plating and Stripping of Sodium from a Room Temperature 1,2-Dimethyl-3-propylimidazolium Chloride Melt", Journal of the Electrochemical Society, 143, 2262 (1996).
51. Rieger, M.M., Dudel, F.P., Pickering, J.P., Gole, J.L., Kohl, P.A., and Bottomley, L.A., "Photoluminescence in the Earliest Stages of Porous Silicon Formation", Journal of The Electrochemical Society, 143, L164 (1996).
52. Lee, J.B., Allen, M.A., Hodge, T.C., Bidstrup, S.A., and Kohl, P.A., "Modeling of Substrate-Induced Anisotropy in Through-Plane Behavior of Polymeric Thin Films", Journal of Polymer Science, Part B, Polymer Physics, 34, 1591-1596, 1996.
53. Kohl, P., Bidstrup, S., and Grove, N., Shick, R., Goodall, B., McIntosh, and L., Jayaraman, S., "New Olefinic Interlevel Dielectric Materials for Microelectronics", Advancing Microelectronics, 24, 16-18, (1996).
54. Gray, G.E., Winnick, J., and Kohl, P.A., "Plating and Stripping of Sodium from a Room Temperature 1-methyl-3-propylimidazolium Chloride Melt" Journal of the Electrochemical Society, 143, 3820-24 (1996).
55. Sullivan, A.M., and Kohl, P.A., "Electrochemical Study of the Gold Thiosulfate Reduction", Journal of the Electrochemical Society, 144, 1686 (1997).
56. Pye, S., Winnick, J., and Kohl, P.A., "Iron, Copper, and Nickel Behavior in Buffered, Neutral Aluminum Chloride: 1-Methyl-3-Ethylimidazolium Chloride Molten Salt", Journal of the Electrochemical Society, 144, 1933-8 (1997).
57. Hodge, T.C., Grove, N.R., Sinno, B., Bidstrup, S.A., and Kohl, P.A., "Stresses of Spin-Cast Polymer Films on Silicon Substrates", Journal of Microcircuits and Electronic Packaging, 20, 12-20 (1997).
58. Hodge, T.C., Bidstrup, S.A., and Kohl, P.A., "Stresses in Thin Film Metals", IEEE Transactions on Components, Packaging, and Manufacturing Technology, 20, 241-250 (1997).
59. Henderson, M. L., Kohl, P.A., Eddy, M., and Zuck, B., "The Performance of Superconducting Microwave Devices Passivated with Dielectric Materials", Applied Physics Letters, 71, 1564 (1997).
60. Kropewnicki, T.J., and Kohl, P.A., "Hydrazine Cyanurate as a Nitrogen Source for Thin Film Nitride Film Growth", Journal of Vacuum Science A, 16, 139 (1998).

61. Sullivan, A.M., and Kohl, P.A., "Electrooxidation of Ascorbic Acid in an Aqueous Citrate Buffer Solution", Plating and Surface Finishing, **85**(2), 56-60 (1998).
62. Patel, K., Kohl, P.A. and Bidstrup, S.A., "Novel Technique for Measuring Through-Plane Modulus in thin Polymer Films", IEEE Journal of Components, Processing and Manufacturing Technology-B, **21**, 199 (1998).
63. Scott, L. L., Ding, Y., Stalder, S. M., Kohl, P. A., Winnick, J., and Bottomley, L. A., "Electrosynthesis of Sodium Hydrosulfite I. Development of an On-Line Process Control Monitor for the Electrosynthesis of Sodium Hydrosulfite", Journal of The Electrochemical Society, **145**, 4052-6 (1998).
64. Ding, Y., Scott, L. L., Stalder, S. M., Kohl, P. A., Winnick, J., and Bottomley, L. A., "Electrosynthesis of Sodium Hydrosulfite II. The Effect of Cathode Material on the Electrosynthesis of Sodium Hydrosulfite", Journal of The Electrochemical Society, **145**, 4057-61 (1998).
65. Zhao, Q. and Kohl, P. A., "Reactive Ion Etching of Silicon Containing Polynorbornenes", Journal of The Electrochemical Society, **145**, 1257-62 (1998).
66. Doolittle, W. A., Kropewnicki, T., Carter-Comen, C., Stock, S., Kohl, P.A., Jokerst, N. M., metzger, R.A., Kang, S., Lee, K., May, G., and Brown, A.S., "Growth of GaN on Lithium Gallate Substrates for Development of a GaN Thin compliant Substrate", Journal of Vacuum Science and Technology B, **16**, 1300 (1998).
67. Kohl, P.A., Zhao, Q., Patel, K.S., Schmidt, D.S., Bidstrup, S.A., Shick, R., and Jayaraman, S., "Air-Gaps for Electrical Interconnections", Electrochemical and Solid State Letters, **1**, 49-51 (1998).
68. Kohl, P.A., "Photoelectrochemical Processing of Semiconductors for Micromachining Applications" IBM Research Journal, **42**, 629-37 (1998).
68. Gole, J. L., Dudel, F. P., Seals, L., Reiger, M., Kohl, P.A., and Bottomley, L. A., "On the Correlation of Aqueous and Nonaqueous In-Situ and Ex-Situ Photoluminescent Emissions from Porous Silicon - Evidence for Surface Bound Emitters", Journal of The Electrochemical Society, **145**, 3284-3300 (1998).
69. Scott, L. L., Ding, Y., Stalder, S. M., Kohl, P. A., Winnick, J., and Bottomley, L. A., "Electrosynthesis of Sodium Hydrosulfite III. Porous Cathode Material and Process Model", Journal of the Electrochemical Society, **145**, 4062-66 (1998).
70. Hodge, T. C., Bidstrup-Allen, S. A., and Kohl, P. A., "In-situ Measurement of the Thermal Expansion Behavior of Benzocyclobutene Films", J. Polymer Science B, **37**, 311-321 (1999).

71. Doolittle, W. A., Kang, S., Kropewnicki, T.J., Stock, S., Kohl, P.A., and Brown, A.S., "MBE Growth of High Quality GaN on LiGaO₂" Journal of Electronic Materials, **27**, L58 (1998).
72. Ahmed, S., Bidstrup, S. A., Kohl, P. A., and Ludovice, P. J., "Development of a New force Field for Polynorbornene", Journal of Physical Chemistry, **102**, 9783-90 (1998).
73. Ahmed, S., Bidstrup, S. A., Kohl, P. A. and Ludovice, P. J. ""Prediction of Stereoregular Poly(norbornene) Structure using a Long-Range RIS Model" Macromol Symp., **133**, 1-10 (1998).
74. Ahmed, S. Bidstrup, S.A., Kohl, P., and Ludovice, P., "Determination of the Stereochemistry of Polynorbornene as a Function of Synthesis Catalyst" Macromolecules, **133**, 1-10 (1998).
75. Manepalli, R., Stepniak, F., Bidstrup, S. A., and Kohl, P. A., "Silver Metallization for Advanced Interconnections", IEEE Transactions on Advanced Packaging, **22**, 4-9 (1999).
76. Kohl, A. T., Rhodes, L., Shick, R., Wong, Z. L., and Kohl, P. A., "Low-k, Porous Methylsilsequioxane and Hydrogensilsequioxane", Electrochemical and Solid-State Letters, **2**, 77 (1999).
77. Kropewnicki, T. J., Doolittle, W. A., Carter-Coman, C. K., Sangboem, Kohl, P. A. Jokerst, N. M., and Brown, A. S., "Selective Wet Etching of Lithium Gallate" Journal of The Electrochemical Society, **145**, L88-L90 (1998).
78. Flake, J. C., Rieger, M. M., Schmid, G. M., and Kohl, P. A., "Electrochemical Etching of Silicon in Nonaqueous Electrolytes Containing Hydrogen Fluoride or Fluorborate", Journal of The Electrochemical Society, **146**, 1960 (1999).
79. Agraharam, S., Hess, D. W., Kohl, P. A., Bidstrup-Allen, S. A., "Plasma Chemistry in Fluorocarbon Film Deposition from Pentafluoroethane/argon Mixtures" Journal of Vacuum Science and Technology A, **17**, 3265-3271 (1999).
80. Grove, N. R., Kohl, P. A., Bidstrup Allen, S. A., Jayaraman, S., and Shick, R., "Functionalized Polynorbornene Dielectric Polymers: Adhesion and Mechanical Properties", Journal of Polymer Science, **37**, 3003-3010 (1999).
81. Rieger, M. M., Flake, J. C., and Kohl, P. A., "Alternatives to Hydrogen Fluoride for Photoelectrochemical Etching of Silicon", Journal of The Electrochemical Society, **146**, 4485 (1999).
82. Manepalli, R., Farnsworth, K. D., Bidstrup Allen, S. A., and Kohl, P. A., "Multi-layer Electron Beam Curing of Polymer Dielectric for Electrical Interconnections", Electrochemical and Solid-State Letters, **3**, 228-231 (2000).

83. Ogitani, S., Bidstrup-Allen, S. A., and Kohl, P. A., "Factors Influencing the Permittivity of Polymer/Ceramic Composites for Embedded Capacitors", IEEE Transactions on Components, Packaging, and Manufacturing Part B, 23, 313-322 (2000).
84. Ahmed, S.; Bidstrup, S.A.; Kohl, P.; Ludovice, P. "Microstructure of 2,3-erythro Di-Isotactic Polynorbornene from Atomistic Simulation" J. Comp. and Theor. Polym. Sci., 10, 221-233 (2000).
85. Patel, K. S., Kohl, P. A., and Bidstrup Allen, "Dual Capacitor Technique for Measurement of Through-Plane Modulus of Thin Polymer Films", Journal of Polymer Science, Polymer Physics, 38, 1634-1644 (2000).
86. Agraharam, S., Hess, D. W., Kohl, P. A., and Allen, S. A., "Thermal Stability of Fluorocarbon Films Deposited from pentafluoroethane/Argon Plasmas", Journal of The Electrochemical Society, 147, 2665-2670 (2000).
87. Farnsworth, K.D., Manepalli, R. N., Bidstrup Allen, S. A., and Kohl, P. A., "Variable Frequency Microwave Curing of 3,3',4,4'- Biphenyltetracarboxylic acid dianhydride / P-Phenylenediamine (BPDA/PPD)", International Journal of Microcircuits and Electronic Packaging, 23, 162-171 (2000).
88. Kohl, P. A., Bhusari, D. M., Wedlake, M., Case, C., Lee, B. C., Gutmann, R. J., and Shick, R., "Air Gaps in 0.3 μm Electrical Interconnections", Electron Device Letters, 21, 557-560 (2000).
89. Park, S. H., Winnick, J. and Kohl, P. A., "Stability of Sodium Couple in Organic and Inorganic Molten Salt Electrolytes Investigated with Electrochemical Quartz Crystal Microbalance", Journal of The Electrochemical Society, 148, A346-A350 (2001).
90. Ogitani, S., Silvestrov, V., Kohl, P. A., and Allen, S. A., "Development of a Ceramic/Epoxy Composite for Embedded Capacitors", International Journal of Microcurcuits and Electronic Packaging, 23, 367-378 (2000).
91. Manepalli, R., Kovach, D. J., Farnsworth, K., Chiniwalla, P., Dusch, B., Bidstrup Allen, S. A., and Kohl, P. A., "Electron Beam Enhanced Multilayering in Preimidized Polyimides", IEEE Transactions on Advanced Packaging, 24, 175-184 (2001).
92. Patel, K. S., Kohl, P. A., and Allen, S.A., "Three-dimensional Dielectric Characterization of Polymer Films", Journal of Applied Polymer Science, 80, 2328-2334 (2001).
93. Su, L., Kohl, P.A., and Winnick, J., "Sodium Insertion into Vanadium Pentoxide in Methanesulfonyl Chloride-Aluminum Chrloride Ionic Liquid", Journal of

- Power Sources, 101, 226-230 (2001).
94. Li, J., Murphy, E., Winnick, J., and Kohl, P.A., "Studies on the Cycle Life of Commercial Lithium Ion Batteries During Rapid Charge-Discharge Cycles", Journal of Power Sources, 102, 294-301 (2001).
 95. Li, J., Murphy, E., Winnick, J., and Kohl, P.A., "The Effects of Pulse Charging on Cycling Characteristics of Commercial Lithium Ion Batteries", Journal of Power Sources, 102, 302-309 (2001).
 96. Bhusari, D., Reed, H., Wedlake, M., Padovani, A., Bidstrup-Allen, S. A., Kohl, P. A., "Fabrication of Air-Channel Structures for Microfluidic, Microelectromechanical and Microelectronic Applications", Journal of Microelectromechanical Systems, 10, 400-409 (2001).
 97. Chiniwalla, P., Manepalli, R., Farnsworth, K., Boatman, M., Dusch, B., Bidstrup Allen, S. A., and Kohl, P. A., "Multilayer Planarization of Polymer Dielectrics", IEEE Transactions on Advanced Packaging, 24, 41-53 (2001).
 98. Agraharam, S., Hess, D. W., Kohl, P.A., and Allen, S. A., "Comparison of Plasma Chemistries and Structure-Property Relationships of Fluorocarbon Films Deposited from Octafluorocyclobutane and Pentafluoroethane Monomers" Journal of Vacuum Science and Technology B, 19, 1071-1023 (2001).
 99. Tanikella, R. V., Allen, S. A., and Kohl, P. A., "Variable Frequency Microwave Curing of Benzocyclobutene", Journal of Applied Polymer Science, 83, 3055-3067 (2002).
 100. Agraharam, S., Hess, D. W., Kohl, P. A., and Allen, S. A., "Electrical Properties and Temperature-Humidity Studies of Fluorocarbon Films Deposited from Pentafluoroethane/Argon Plasmas", Journal of The Electrochemical Society, 148, F102-F107 (2001).
 101. Reed, H. A., White, C. E., Rao, V., Allen, S. A., Henderson, C. L., and Kohl, P. A., "Fabrication of Microchannels Using Polycarbonates as Sacrificial Materials", Journal of Micromechanics and Microengineering, 11, 733-737 (2001).
 102. Tanikella, R. V., Agraharam, S., Allen, S. A., Hess, D. W., and Kohl, P. A., "Moisture Absorption Studies of Fluorocarbon Films Deposited from Pentafluoroethane and Octafluorocyclobutane Plasmas" Journal of Electronic Materials, 31, 1096-1103 (2002).
 103. Fansworth, K. D., Manepalli, R. N., Allen, S. A., and Kohl, P. A., "Variable Frequency Curing of Photosensitive Polyimides", IEEE Components and Packaging Technologies, 24, 474-481 (2001).
 104. Rao, Y., Ogitali, S., Kohl, P., and Wong, C.P., "Novel Polymer-Ceramic

Nanocomposite Epoxy Formula for Embedded Capacitor Applications", Journal of Applied Polymer Science, **83**, 1084-1090 (2002).

105. Padovani, A., Rhodes, L, Riester, L, Lohman, G., Tsuie, B., Conner, J., Allen, S. A., and Kohl, P. A., " Porous Methylsilsesquioxane for Low- k Dielectric Applications" Electrochemical and Solid-State Letters, **4**, F25-F28 (2001).
106. Park, S., Moore, C. W., Kohl, P. A., and Winnick, J., "A Study of Copper as a Cathode Material for an Ambient Temperature Sodium Ion Battery", Journal of The Electrochemical Society, **148**, A1346-A1351 (2001).
107. Wedlake, M. D. and Kohl, P. A., "Thermal Decomposition Kinetics of Polynorbornene", Journal of the Materials Research Society, **17**, 632-640 (2002).
108. Meindl, J. D., Davis, J. A., Zarkesh-Ha, P., Patel, C., Martin, K., and Kohl, P. A., "Interconnect Opportunities for Gigascale Integration", IBM Research Journal, **46**, 245-265 (2002).
109. Chinthakindi, A. K., Bhusari, D., Dusch, B. P., Musolf, J., Willemsen, B. A., Prophet, E., Roberson, M, and Kohl, P. A., " Electrostatic actuators with intrinsic stress gradient. Part-I. Materials and Structures" Journal of The Electrochemical Society, **149**, H139-H145 (2002).
110. Chinthakindi, A. K., and Kohl, P. A., " Electrostatic actuators with intrinsic stress gradient. Part-II. Modeling and Properties" Journal of The Electrochemical Society, **149**, H146-H152 (2002).
111. Park, S. H., Winnick, J., and Kohl, P. A., "Investigation of the Lithium Couple on Pt, Al, and Hg Electrodes in Lithium Imide-Ethyl Methyl Sulfone", Journal of The Electrochemical Society, **149**, A1196-A1200 (2002).
112. Wu, X., Reed, H. R., Rhodes, L. F., Elce, E., Ravikiran, R., Shick, R. A., Henderson, C. L., Allen, S. A., and Kohl, P. A., "Lithographic Characteristics and Thermal Processing of Photosensitive Sacrificial Materials", Journal of The Electrochemical Society, **149**, G555-G561 (2002).
113. Chinthakindi, A. K., Bhusari, D., Dusch, B. P., and Kohl, P. A., "Recrystallization and Intermetallic Formation in Au/Al and Au/Zn Bimetallic Films", Journal of Electronic Materials, **31**, 1096-1103 (2002).
114. Wu, X, Reed, H. A., Rhodes, L., Elce, E., Ravikiran, R., Shick, R.A., Henderson, C. L., Allen, S. A., and Kohl, P. A., "Photoinitiation Systems and Thermal Decomposition of Photodefinable Sacrificial Materials", Journal of Applied Polymer Science, **88**, 1186-1195 (2003).
115. Li, J., and Kohl, P.A., "The Acceleration of Non Formaldehyde Electroless Copper Plating", Journal of The Electrochemical Society, C631-C636 (2002).

116. Padovani, A. M., Rhodes, L., Allen, S. A., and Kohl, P. A., "Chemically Bonded Porogens in Methylsilsesquioxane, Part I: Structure and Bonding" Journal of The Electrochemical Society, 149, F161-F170 (2002).
117. Padovani, A. M., Riestler, L., Rhodes, L., Allen, S. A., and Kohl, P. A., "Chemically Bonded Porogens in Methylsilsesquioxane, Part II: Electrical, Optical, and Mechanical Properties" Journal of The Electrochemical Society, 149, F171-F180 (2002).
118. Chiniwalla, P., Bai, Y., Elce, E., Shick, R. A., Allen, S. A., and Kohl, P. A., "Crosslinking and Decomposition Reactions of Epoxide Functionalized Polynorbornene: Part 1: FTIR and Thermogravimetric Analysis", Journal of Applied Polymer Science, 89, 568-577 (2003).
119. Jayachandran, J. P., Reed, H. A., Zhen, H., Bidstrup Allen, S. A., and Kohl, P. A., "Air-channel Fabrication for Microelectromechanical Systems Via Sacrificial Photosensitive Polycarbonates", Journal of Microelectromechanical Systems, 12, 147-160 (2003).
120. Li, W., Tegenfeldt, J. O., Chen, L., Austin, R. H., Chou, S. Y., Kohl, P. A., Krotine, J. and Sturm, J. C., "Sacrificial Polymers for Nanofluidic Channels in Biological Applications", Nanotechnology, 14, 578-583 (2003).
121. Wu, X., Reed, H. A., Wang, Y., Rhodes, L. F., Elce, E., Ravikiran, R., Shick, R. A., Henderson, C. L., Allen, S. A., and Kohl, P. A., "Fabrication of Microchannels using Polynorbornene Photosensitive Sacrificial Materials", Journal of The Electrochemical Society, 150, H205 (2003).
122. Li, Jun, and Kohl, P. A., "The Deposition and Characteristics of Accelerated Nonformaldehyde Electroless Copper Plating", Journal of The Electrochemical Society, 150, C558 (2003).
123. Bakir, M. S., Reed, H. A., Thacker, H. D., Patel, C. S., Kohl, P. A., Martin, K.P., and Meindl, "Sea-of-Leads Ultrahigh Density Wafer-Level Input/Output Interconnections for Giga-scale Integration (GSI)", IEEE Transactions on Electron Devices, 50, 2039-2049 (2003).
124. Bai, Y., Chiniwalla, P., Elce, E., Shick, R. A., Sperk, J., Allen, S. A., and Kohl, P. A., "Photosensitive Polynorbornene Based Dielectric: Part I, Structure-Property Relationships", Journal of Applied Polymer Science, 95, 3023-3030 (2004).
125. Bai, Y., Chiniwalla, P., Elce, E., Allen, S. A., and Kohl, P. A., "Photosensitive Polynorbornene Based Dielectric: Part II, Sensitivity and Spatial Resolution", Journal of Applied Polymer Science, 95, 3031-3039 (2004).
126. Gray, G., Morgan, M., and Kohl, P. A., "Electrostatic Actuators with Expanded

- Tuning Range Due to Intrinsic Stress Gradients", IEEE Microelectromechanical Systems, **13**, 51-63 (2004).
127. Chiniwalla, P., Bai, Y., Elce, E., Shick, R. A., Allen, S. A., and Kohl, P. A., "Crosslinking and Decomposition Reactions of Epoxide Functionalized Polynorbornene: II Impact of Reactions on Mechanical Properties", Journal of Applied Polymer Science, **91**, 1020-1029 (2003).
 128. Li, J., Haden, H., and Kohl, P. A., "The Influence of 2,2'-Dipyridyl on Non-formaldehyde Electroless Copper Plating", Electrochimica Acta, **49**, 1789-1795 (2004).
 129. Li, J., and Kohl, P. A., "Complex Chemistry and the Electroless Copper Plating Process", Plating and Surface Finishing, **91**, 40-3 (2004).
 130. Salas-Vernis, J. L., Jayachandran, J. P., Park, S., Kelleher, H. A. Allen, S. A., and Kohl, P. A., "Hydrophobic/Hydrophilic Surface Modification Within Buried Air-Channels", Journal of Vacuum Science and Technology-B, **22**, 935-960 (2004).
 131. Kim, K., Lang, C., Moulton, R., and Kohl, P. A., "Electrochemical Investigation of Quaternary Ammonium/Aluminum Chloride Ionic Liquids", Journal of The Electrochemical Society, **151**, A1168-72 (2004).
 132. Dusch, B., and Kohl, P. A., "Planarization and Dielectric Properties of Thin Photosensitive and Nonphotosensitive BCB", Journal of Microelectronics and Electronic Packaging, **1**, 47-53 (2004).
 133. He, A., Allen, S. A., and Kohl, P. A., "Nano-imprinting of Optical Gratings", Electrochemical and Solid-State Letters, **7**, F55-8 (2004).
 134. Kim, K., Lang, C., and Kohl, P. A., "The Role of Additives In the Electroreduction of Sodium Ions in Chloroaluminate-based Ionic Liquids", Journal of The Electrochemical Society, **152**, E9-13 (2005).
 135. Li, J., Moore, C., and Kohl, P. A., "Investigation of Acidic Methanol Solution as a Fuel for Micro-channel Fuel Cells" Journal of Power Sources, **138**, 211-5 (2004).
 136. Sundaram, V., Tummala, R. R., Kohl, P. A., Li, J., Allen, S. A., and Fukuoka, Y., "Next Generation Microvia and Global Interconnect Technologies for SOP", IEEE Transactions on Advanced Packaging, **27**, 315-325 (2004).
 137. Joseph, P. J., Kelleher, H. A., Allen, S. A., and Kohl, P. A., "Improved Fabrication of Micro Air-channels by Incorporation of a Structural Barrier", Journal of Micromachining and Microengineering, **15**, 35-42 (2004).
 138. Gray, G. D., and Kohl, P. A., "Magnetically Bistable Switch, Part I: Modeling and Ultra Low Switching Energy", Sensors and Actuators A, **119**, 489-501 (2005).

139. Gray, G. D., Prophet, E. M., Zhu, L., and Kohl, P. A., "Magnetically Bistable Switch, Part II: Fabrication and Performance", Sensors and Actuators A, **119**, 502-511 (2005).
140. Mule' A. V., Villalaz, R., Jayachandran, J. P., Kohl, P. A., Gaylord, T. K., and Meindl, J. D., "Polyolithic Integration of Electrical and Optical Interconnect Technologies for CMOS GSI", IEEE Transactions on Advanced Packaging, **28**, 421-433 (2005).
141. Kim, K., Lang, C., and Kohl, P. A., "Properties of Asymetric Benzyl-substituted Quaternary Ammonium Ionic Liquids", Journal of The Electrochemical Society, **152**, E56-60 (2005).
142. Sung, T., Allen, S. A., and Kohl, P. A., "Low Temperature Rapid Curing of Polymer Dielectrics on Metallized Organic Laminates by Variable Frequency Microwave Processing", Journal of Microelectronics and Electronic Packaging, **2**, 142-154 (2005).
143. Tanikella, R., Sung, T., Allen, S. A., and Kohl, P. A., "Rapid Curing of Positive Tone Photosensitive Polybenzoxazole Based Dielectric Resin by Variable Frequency Microwave Processing", IEEE Packaging, Components Manufacturing Technology, **29**, 411-419 (2006).
144. Park, S. H., Krotine, J., Allen, S. A., and Kohl, P. A., "Electron-beam Hardening of Thin Films of Functionalized Polynorbornene Copolymer", Journal of Electronic Materials, **35**, 1112-1121 (2006).
145. Bhusari, D., Li, J., Joseph, P., Moore, C., and Kohl, P. A., "Development of P-doped SiO₂ as Proton Exchange Membrane for Micro-Fuel Cells.", Electrochemical and Solid-State Letters, **8**, A588-591 (2005).
146. Lang, C. M., Kim, K., Guerra, L., and Kohl, P. A., "Cation Electrochemical Stability in Chloroaluminate Ionic Liquids", Journal of Physical Chemistry B, **109**, 19454-19462 (2005).
147. Bhusari, D., Haden, H., Tanikella, R., Allen, S. A., and Kohl, P. A., "Plasma Treatment and Surface Analysis of Polyimide Films for Electroless Copper Build-up Process", Journal of The Electrochemical Society, **152**, F162-F170 (2005).
148. Moore, C. W., Li, J., and Kohl, P. A., "Microfabricated Fuel Cells with Silicon Dioxide Proton Exchange Membranes", Journal of The Electrochemical Society, **152**, A1606 (2005).
149. Gray, G. D., and Kohl, P. A., "Modeling and Performance of a Magnetic MEMS Wiping Actuator", Journal of Microelectromechanical Systems, **15**, 904-912 (2006).

150. Arepalli, S., Fireman, H., Huffman, P., Moloney, P., Nikolaey, P., Yowell, L. Higgins, C. D., Kim, K., Kohl, P. A., Turano, S.P., and Ready, W. J., "Carbon-Nanotube-Based Electrochemical Double-Layer Capacitor Technologies for Spaceflight Applications, Journal of Materials (JOM), 57(12), 26-31 (2005).
151. Bakir, M., Dang, B., Emery, R., Vandentop, G., Kohl, P. A., and Meindl, J. D., "Sea of Leads Compliant I/O Interconnect Process Integration for the Ultimate Enabling of Chips with Low-k Interlayer Dielectrics", IEEE Transactions on Components, Packaging, and Manufacturing Technology, B Advanced Packaging, 28, 488-494 (2005).
152. Li, J., Moore, C. W., Bhusari, D., Prakash, S., and Kohl, P. A., "Microfabricated Fuel Cells with Composite Proton Exchange Membranes", Journal of The Electrochemical Society, 153, A343-347 (2006).
153. Lang, C. M., Kim, K., and Kohl, P. A., "Catalytic Additives for the Reversible Reduction of Sodium in Chloroaluminate Ionic Liquids", Electrochimica Acta, 51, 3884-3889 (2006).
154. Doyle, K., Lang, C., Kim, K., and Kohl, P. A., "Dendrite Free Electrochemical Deposition of Li-Na Alloys from an Ionic Liquid Electrolyte", Journal of The Electrochemical Society, 153, A1353-7 (2006).
155. Glebov, A. L., Bhusari, D., Kohl, P. A., Bakir, M., Meindl, J. M., and Lee, M. G., "Flexible Pillars for Displacement Compensation in Optical Chip Assembly", IEEE Photonics Technology Letters, 18, 974-976 (2006).
156. Monajemi, P., Joseph, P. J., Kohl, P. A., and Ayazi, F., "Wafer-level MEMS packaging via thermally released metal-organic membranes", Journal of Micromechanics and Microengineering, 16, 742-750 (2006).
157. Lang, C., Kim, K., and Kohl, P. A., "High Energy Density, Room Temperature Carbonate Fuel Cell", Electrochemical and Solid-State Letters, 9, A545-A549 (2006).
158. He, A., Osborn, T., Bidstrup Allen, S.A., and Kohl, P. A. "Low-Temperature Bonding of Copper Pillars for All-Copper Chip-to-Substrate Interconnections", Electrochemical and Solid-State Letters, 9, C192-C195 (2006).
159. Joseph, P., Pejman, M., Ayazi, F., and Kohl P. A., "Wafer Level Packaging of MEMS Resonators", IEEE Transactions on Advanced Packaging, 30, 19-26 (2007).
160. Abdallah, J., Silver, M., Allen, S. A., and Kohl, P. A., "UV-initiated Directly-Write Porosity using Photoacid-Catalyzed Decomposition of Sacrificial Polymers Templated in Dielectric Films", Journal of Materials Chemistry, 17, 873-885

(2007).

161. Gupta, M., Joseph, P., and Kohl, P. A., "Photoacid Generators for Catalytic Decomposition of Polycarbonates", Journal of Applied Polymer Science, **105**, 2655-2662 (2007).
162. Tanaka, K., Allen, S. A., and Kohl, P. A., "Variable Frequency Microwave Curing of Amide-Epoxy Based Polymers", IEEE Transactions on Components and Packaging Technologies, **30**, 472-477 (2007).
163. Lang, C, and Kohl, P. A. "Investigation of Ether Substituted Quaternary Ammonium Ionic Liquids", Journal of The Electrochemical Society, **154**, F106-F110 (2007).
164. Spencer, T. J., Joseph, P., Kim, T. H., Swaminathan, M., and Kohl, P. A., "Air-gap transmission lines on organic substrates for low-loss multiprocessor interconnects", IEEE Transactions on Microwave Theory and Techniques, **55**, 1919-1925 (2007).
165. Mustain, W. E., Kim, H., Prakash, S., Stark, J., Osborn, T., and Kohl, P. A., "Platinum-Glass Composite Electrode for Fuel Cell Application", Electrochemical and Solid-State Letters, **10**, B210-B213 (2007).
166. Prakash, S., Mustain, W., Park, S., and Kohl, P. A., "Phosphorus-Doped Glass Proton Exchange Membranes for Low Temperature Direct Methanol Fuel Cells" Journal of Power Sources, **175**, 91-97 (2008).
167. Osborn, T., He, A., Galiba, N., and Kohl, P. A., "All-Copper Chip-to-Substrate Interconnects, Part I: Fabrication and Characterization", Journal of The Electrochemical Society, **155**, D308-D313 (2008).
168. He, A., Osborn, T., Allen, S. A., and Kohl, P. A., "All-Copper Chip-to-Substrate Interconnects, Part II: Modeling and Design", Journal of The Electrochemical Society, **155**, D314-D322 (2008).
169. Bakir, M., Glebov, A., Lee, M., Kohl, P. A., and Meindl, J. D., "Mechanically Flexible Chip-to-Substrate Optical Interconnections Using Optical Pillars", IEEE Transactions on Advanced Packaging, **31**, 143-153 (2008).
170. Davis, S., Gray, G, and Kohl, P. A., "Electrochemical Salt-Splitting of Sodium Sulfate", Journal of Applied Electrochemistry, **38**, 777-783 (2008).
171. Rais-Zadeh, M., Kohl, P. A., and Ayazi, F., "MEMS Switched Tunable Inductors", Journal of Microelectromechanical Systems, **17**, 78-84 (2008).
172. Spencer, T., Osborn, T., and Kohl, P. A., "High Frequency Chip Connections", Science, **320**, 756-7 (2008).

173. Park, S., Allen, S. A., and Kohl, P. A., "Air-Gaps for High Performance On-Chip Interconnect, Part I: Improvement in Thermally Decomposable Template", Journal of Electronic Materials, 37, 1524-33 (2008).
174. Park, S., Allen, S. A., and Kohl, P. A., "Air-Gaps for High Performance On-Chip Interconnect, Part II: Modeling, Fabrication, and Characterization", Journal of Electronic Materials, 37, 1534-46 (2008).
175. Prakash, S., Mustain, W., and Kohl, P. A., "Carbon Dioxide Vent for Direct Methanol Fuel Cells", Journal of Power Sources, 185, 293-400 (2008).
176. Mustain, W., Kim, H., Osborn, T., and Kohl, P. A., "Deposition of Pt_xRu_{1-x} Catalysts for Methanol Oxidation in Micro Direct Methanol Fuel Cells", Israel Journal of Chemistry, 48, 251-259 (2008).
177. Hayden, H., Allen, S. A., and Kohl, P. A., "Adhesion Enhancement Between Electroless Copper and Epoxy-Based Dielectrics", IEEE Transactions on Advanced Packaging, in-press.
178. Zhou, J., Unlu, M., and Kohl, P. A., "Anionic Polysulfone Ionomers and Membranes Containing Fluorenyl Groups for Anionic Fuel Cells", Journal of Power Sources, in-press.
179. Prakash, S., Mustain, W., and Kohl, P. A., "Performance of Li-Ion Secondary Batteries in Low-Power, Hybrid Power Supplies" Journal of Power Sources, in-press.
180. Unlu, M., Zhou, J., and Kohl, P. A., "Anionic Membrane Fuel Cells: Experimental Comparison of Hydroxide and Carbonate Conductive Ions" Electrochemical and Solid-State Letters, in-press.
181. Vega, J., Zhou, J., and Kohl, P. A., "Electrochemical Comparison and Deposition of Lithium and Potassium from Phosphonium- and Ammonium-TFSI Ionic Liquids", Journal of The Electrochemical Society, in-press.

Patents Granted

1. Spray Cell for Selective Metal Deposition or Removal. R.R. Buckley and P.A. Kohl, Patent Number: 4,229,269.
2. Preventing Stains on Multiple Electroplated Articles. P.A. Kohl, Patent Number: 4,236,976.

3. Solder Plating Process. P.A. Kohl, Patent Number: 4,263,106.
4. Electrolytic Plating. P.A. Kohl, Patent Number: 4,310,392.
5. Photoelectrochemical Etching of Semiconductors. P.A. Kohl and F.W. Ostermayer, Patent Number: 4,369,099.
6. Photoelectrochemical Gold Plating Process. R.R. Buckley, L.A. D'Asaro, P.A. Kohl, F.W. Ostermayer, and C. Wolowodiuk, Patent Number: 4,399,004.
7. Electrolytic Gold Plating. P.A. Kohl, Patent Number: 4,377, 448.
8. Photoelectrochemical Processing of InP type Devices. P.A. Kohl, F.W. Ostermayer, and C. Wolowodiuk, Patent Number: 4,389,291.
9. Photoelectrochemical III-V Semiconductor Processing of Compound Semiconductors. P.A. Kohl and F.W. Ostermayer, Patent Number: 4,404,072.
10. Electrolytic Plating of Zinc. P.A. Kohl, Patent Number: 4,379,738.
11. Photoelectrochemical Plating of Silver. J.R. Bessette and Paul Kohl, Patent Number: 4,425,196.
12. Electrochemical Photoetching of Compound Semiconductors. S.R. Forrest, P.A. Kohl and R.L. Panock, Patent Number: 4,414,066.
13. Fabrication of Cleaved Semiconductor Lasers. C.A. Burrus, P.A. Kohl, T.P. Lee and F.W. Ostermayer, Patent Number: 4,689,125.
14. Electrolytic Deposition of Nickel. P.A. Kohl, Patent Number: 4,376,018.
15. Etching of Optical surfaces. R.H. Burton, P.A. Kohl and F.W. Ostermayer Jr., Patent Number: 4,415,414.
16. Photoelectrochemical Etching of n-Si. D.E. Bacon, J.R. Bassette and P.A. Kohl, Patent Number: 4,482,443.
17. Etching Optical surfaces on GaAs. P.A. Kohl, L.E. Smith, H.S. Trop, Patent Number: 4,576,691.
18. Electrolytic Silver Plating, P.A. Kohl, Patent Number: 4,377,449.
19. Photoelectrochemical Etching of n-Type Gallium Arsenide. Patent Number: 4,482,442.
20. Semiconductor Laser with Photoelectrochemically Produced Gratings, P.A. Kohl, R.M. Lum, and F.W. Ostermayer Jr., Patent Number: 4,622,114.

21. Aligning arrays of Optoelectronic Devices to Arrays of Optical Fibers, Brown, M., Forrest, S., Kaplan, D., Kohl, P. A., Ito, Y., and Trop, H., 4,730,198.
22. System for Photoelectrochemical Etching of Silicon in an Anhydrous Environment, Kohl, P. A., 5,431,766.
23. Non-Aqueous Etching of Silicon, Kohl, P.A., and E. Propst, Patent Number: 5,348,627.
24. Low Temperature Passivation of Metals and Semiconductors, Kohl, P.A., and Vogt, K., Patent Number: 5,468,688.
25. Fabrication of Semiconductor Device with Air Gaps for Ultra-Low Capacitance Interconnections, P.A. Kohl, Q. Zhao, and S.A. Bidstrup, U.S. Patent #6,165,890.
26. System and method for Efficient Manufacturing of Liquid Crystal Displays, Drabik, T., Kohl, P.A., Patent #6,141,072.
27. Porous Insulating Compounds and Method for Making Same, Kohl, P. A., U.S. Patent #6,162,838.
28. Porous Insulating Compounds and Method for Making Same, Kohl, P. A., Patent #6,509,386.
29. System and Method for Efficient Manufacturing of Liquid Crystal Displays, Drabik, T., and Kohl, P. A., Patent #6,469,761.
30. Fabrication of Semiconductor Device with Air Gaps for Ultra Low Capacitance Interconnections and Methods, Kohl, P. A., Allen, S. A., Henderson, C., Reed, H. A., and Bhusari, D., Patent #6,610,593.
31. Electrostatic Actuators with Intrinsic Stress Gradient, Kohl, P. A. and Musolf, J, Patent #6,625,004.
32. Compliant Wafer-Level Packaging Devices and Methods of Fabrication, Bakir, M., Reed, H., Kohl, P. A., Patel, C. S., Martin, K., and Meindl, J., 6,690,081.
33. Guided Wave Optical Interconnect Within a Compliant Wafer-Level Package, Mule, T., Patel, C., Meindl, J., Gaylord, T., Glytsis, E., Martin, K., Schultz, S., Bakir, M., Reed, H., and Kohl, P., 6,785,458.
34. Backplane, Printed Wiring Board, and/or Multi-chip Module-level Optical Interconnect Layer having Embedded Air-gap Technologies and Methods of Fabrication, Mule, T., Patel, C., Meindl, J., Kohl, P. A., Scholtz, S. M., Gaylord, T., Glytsis, E., Villalaz, R., Bakir, M., and Reed, H., 6,788,867.

35. Optical Waveguides with Embedded Air-gaps Cladding Layer and Methods of Fabrication Thereof, Mule, T., Meindl, J., and Kohl, P. A., 6,807,352.
36. Improved Electroless Plating of Copper, Li, J., and Kohl, P. A., 6,875,474.
37. Fabrication of Semiconductor Devices with Air Gaps for Ultra-Low Capacitance Interconnections and Methods of Making Same, Kohl, P. A., Allen S. A., Henderson, C. and Bhusari, D., #6,888,249.
38. Musolf, J, and Kohl, P. A., "Method of making an electrostatic actuator" #6,933,165
39. Optical waveguides formed from nano air-gap inter-layer dielectric materials and methods of fabrication thereof, Mule', T, Kohl, P. A., Meindl, J. D., Gaylord, T., Glytsis, E., and Allen, S., 6,947,651.
40. Guided-wave optical interconnections embedded within a microelectronic wafer-level batch package, Mule', T., Patel, C., Meindl, J., Gaylord, T., Glytsis, E., Martin, K., Schultz, S., Bakir, M., Reed, H., and Kohl, P. A., 6, 954,576.
41. Sacrificial compositions, methods of use thereof, and methods of decomposition thereof", Kohl, P. A., Joseph, P., Reed, H., Allen, S. A., Henderson, C., and White, C., 7,052,821.
42. Microstructure and Methods of Fabrication thereof, Joseph, P. Kohl. P.A., and Allen, S.A., 7,182,875 (2007).
43. Sacrificial compositions and methods of fabricating a structure using sacrificial compositions, Kohl, P. A., Jayachandran, P., Reed, H., Allen, S., White, C., and Henderson, C., 7,459,267 (2008).
44. Fabrication of a semiconductor device with air gaps for ultra-low capacitance interconnections, Kohl, P.A. Zhao, Q, and Allen, S.A., #7,504,699 (2009).

Editorial and Reviewer Work for Technical Journals

1. Divisional Editor for the Electrochemical Society

2. Reviewer for:

Applied Physics Letters
Journal of the American Chemical Society
Journal of Applied Physics
Journal of Physical Chemistry
Journal of the Electrochemical Society

Journal of Electronic Materials
Journal of the Materials Research Society
Electrochimica Acta
National Science Foundation
Department of Energy
Board of Regents, State of Louisiana
IEEE Transactions on Electron Devices
AIChE Journal
IEEE Microelectromechanical Systems
Electrochemical and Solid-State Letters
Science Foundation of Ireland

3. Publication Committee of the Journal of the Electrochemical Society
4. Editor (Founding Editor) of The Electrochemical Society Interface, 1992-1995.
5. Editor-in-Chief, Journal of The Electrochemical Society, 1995-present.
6. Editor-in-Chief (Founding Editor), Electrochemical and Solid-State Letters, 1998-2003.

GEORGIA TECH RESEARCH CORPORATION
OFFICE OF TECHNOLOGY LICENSING
GEORGIA INSTITUTE OF TECHNOLOGY

CONFIDENTIAL AND PROPRIETARY

INVENTION DISCLOSURE

Login Date:

4/12/01

GTRC ID:

2445

1 Title of Invention:

Three-Dimensional Microfluidic Device
Fabrication

2 Short Title:

3 Inventors (Please include all inventors; Use additional sheets as necessary)

Full Name	<u>Paul A. Kohl</u>
Title	<u>Regents' Professor</u>
Dept and MC	<u>ChE 0100</u>
Building, Room	<u>B.H.</u>
Office Phone	<u>404-894-2893</u>
Fax	<u>-2866</u>
Email	<u>paul.kohl@che.gatech.edu</u>
Citizenship	<u>USA</u>
Home Address	<u>130 Cameron Glen Dr.</u> <u>Atlanta, GA 30328</u>
Home Phone	<u>770-951-9324</u>
Contribution %	<u>25%</u>
SSN	

Full Name	<u>Sue Ann Bidstrup Allen</u>
Title	<u>Professor</u>
Dept and MC	<u>ChE 0100</u>
Building, Room	<u>Bunger Henry</u>
Office Phone	<u>404-894-2872</u>
Fax	<u>404-894-2866</u>
Email	<u>sue.bidstrup@che.gatech.edu</u>
Citizenship	<u>USA</u>
Home Address	<u>425 West Spalding Drive</u> <u>Atlanta GA 30328</u>
Home Phone	<u>770-392-9202</u>
Contribution %	<u>25%</u>
SSN	

Full Name	<u>Xiaojun Wu</u>
Title	<u>Post-doctoral Fellow</u>
Dept and MC	<u>ChE 0100</u>
Building, Room	<u>B.H.</u>
Office Phone	<u>404-894-9423</u>
Fax	<u>-2866</u>
Email	<u>xw12@prism.gatech.edu</u>
Citizenship	<u>P.R. China</u>
Home Address	<u>500 Northside Cir.</u> <u>Apt # CC-4, Atlanta, GA 30309</u>
Home Phone	<u>404-355-1210</u>
Contribution %	<u>25%</u>
SSN	

Full Name	<u>Clifford Lee Henderson</u>
Title	<u>Assistant Professor</u>
Dept and MC	<u>ChE 0100</u>
Building, Room	<u>Bunger Henry Room 408</u>
Office Phone	<u>404-385-0525</u>
Fax	<u>404-894-2866</u>
Email	<u>cliff.henderson@che.gatech.edu</u>
Citizenship	<u>USA</u>
Home Address	<u>150 Jackson Bank Place NW</u> <u>Lilburn GA 30047</u>
Home Phone	<u>770-717-1933</u>
Contribution %	<u>25%</u>
SSN	

Full Name:		Citizenship:	
Title:		SSN:	
Department:	Mail Code:	Contribution %:	
Office Address:		Home Address:	
Phone: ()		Phone: ()	
Fax: ()		Fax: ()	
Email:		Email:	
Execution by Inventor(s): I/we inventor(s) hereby solemnly swear and affirm under oath that I/we am/are the only inventor(s) of this invention and that I/we have not knowingly omitted the inclusion of any other inventor(s) besides me/us, and that the information provided in this disclosure is, to the best of my/our knowledge, true and accurate.		Signature: _____ Date: _____	

Full Name:		Citizenship:	
Title:		SSN:	
Department:	Mail Code:	Contribution %:	
Office Address:		Home Address:	
Phone: ()		Phone: ()	
Fax: ()		Fax: ()	
Email:		Email:	
Execution by Inventor(s): I/we inventor(s) hereby solemnly swear and affirm under oath that I/we am/are the only inventor(s) of this invention and that I/we have not knowingly omitted the inclusion of any other inventor(s) besides me/us, and that the information provided in this disclosure is, to the best of my/our knowledge, true and accurate.		Signature: _____ Date: _____	

Invention Description	
Brief Description: (please attach more detailed descriptions, any support materials, reports) <div style="text-align: center; font-size: 1.2em; font-family: cursive;">See attached.</div>	

Source of Support	
Did this invention result from sponsored research? <input checked="" type="checkbox"/> Yes <input type="checkbox"/> No E-19-Y06 If NO, how was this work funded, including salaries, charges of time, materials, supplies, equipment? If YES, please provide information on all: <div style="display: flex; justify-content: space-between;"> <div>Sponsor:</div> <div>GIT Project Number:</div> </div> <div style="display: flex; justify-content: space-between;"> <div>Sponsor:</div> <div>GIT Project Number:</div> </div> Was this project conducted through or associated with a Georgia Tech Center? <div style="display: flex; justify-content: space-between;"> <div><input type="checkbox"/> Yes <input checked="" type="checkbox"/> No</div> <div>If YES, list name of Center.</div> </div> Did you use any material obtained from another party in developing this technology? <div style="display: flex; justify-content: space-between;"> <div><input type="checkbox"/> Yes <input checked="" type="checkbox"/> No</div> <div>If YES, please list source: (attach copy of material transfer agreement if applicable)</div> </div>	

Establishment of Invention History			
❖ Please provide your best estimate for the date when the following occurred (will occur):			
Date(s):	A. Conception of invention 7/24/00 PKC		
	B. First written description (please attach a copy if available) see attached		
	C. First oral disclosure To whom: Paper is being submitted.		
	D. First disclosure outside of Georgia Tech (e.g. abstract, proposal, paper submission, talk, or meeting with industry – please attach a copy if available) To whom:		
	E. Completion of model or prototype		
	F. First successful operational test:		
G. Is a publication or other disclosure planned within 6 months? <input type="checkbox"/> Yes <input type="checkbox"/> No			
If YES, Disclosure Date:		Type of disclosure:	
Prior Art			
❖ Inventors are highly encouraged to conduct a literature and patent search. Two useful sites are: 1) www.uspto.gov and 2) www.surfi.gov.sg			
A. Has a patent or literature been conducted? <input type="checkbox"/> Yes <input type="checkbox"/> No			
B. Are there any related patents or publications known to you? <input type="checkbox"/> Yes <input type="checkbox"/> No			
If Yes, please attach copies or reference list.			
Commercialization Potential			
A. What are the immediate and/or future applications for the invention?			
B. What are the limitations that must be overcome prior to practical application?			
C. What are the advantages of the invention versus present technologies?			
D. Please provide any available data or information on market potential/size.			
E. Is work on the invention continuing? <input type="checkbox"/> Yes <input type="checkbox"/> No			
F. Do you know of any appropriate industrial organizations that may be interested in licensing this technology? (Please attach additional sheet if more space is required.)			
Company Name	Contact Person	Contact Information	
Execution by Witnesses			
❖ This disclosure should be witnessed by two individuals who are not co-inventors and who are technically qualified to understand the subject matter.			
	Print Name	Signature	Date
I have read this invention disclosure (including attached pages, if any) and understand its subject matter.			
I have read this invention disclosure (including attached pages, if any) and understand its subject matter.			

Execution by Inventor(s).

I/We inventor(s) hereby solemnly swear and affirm under oath that I/we am/are the only inventor(s) of this invention and that I/we have not knowingly omitted the inclusion of any other inventor(s) besides me/us, and that the information provided in this disclosure is, to the best of my/our knowledge, true and accurate.

Signature(s) of inventor(s) and date:

Helt
 Luc & Bedstrup alle
 Haage 2bn
 Alfors 2 Benders

Date 2/3/2001

Date 2/5/2001

Date _____

Date 2/6/2001

Date _____

Execution by Witnesses

This invention was disclosed and explained to me by the inventor(s) whose signature(s) appears above on the _____ day of _____, 20____.

Signature of Witness

Date: 2-7-01

This invention was disclosed and explained to me by the inventor(s) whose signature(s) appears above on the _____ day of _____, 20____.

Brian Wagner
Signature of Witness

Date: 2-7-01

Return this form (with any attachments) to the Office of Technology Licensing,
GTRC, Centennial Research Building, Room 275, 400 Tenth Street, Atlanta, GA 30332-0415.

If you have any questions please call (404) 894-6287.

GEORGIA TECH RESEARCH CORPORATION
PROPRIETARY INFORMATION

Fabrication of Microchannels using Polynorbornene Photosensitive Sacrificial

Materials

Xiaoqun Wu^a, Hollie A. Reed^a, Yong Wang^a, Larry F. Rhodes^b, Ed Elce^b, R. Ravikiran^b, Robert A. Shick^b,
Clifford L. Henderson^a, Sue Ann Bidstrup Allen^a, and Paul A. Kohl^{a*}

a: School of Chemical Engineering, Georgia Institute of Technology, Atlanta, Georgia 30332-0100

b: Promerus LLC, 9921 Brecksville Road, Brecksville, OH 44141

ABSTRACT

A processing method has been demonstrated for the fabrication of microchannels by using photosensitive polynorbornene copolymer based sacrificial materials. The channel geometric patterns of sacrificial polymer were made via photolithography. The sacrificial polymer patterns were encapsulated with a dielectric medium and then thermally decomposed to form air channels. For the thermal decomposition of sacrificial polymer, the heating program was determined on the basis of the kinetic model obtained from TGA analysis to maintain the decomposition at a constant rate. The results indicate that a properly selected heating program can avoid the deformation in the channel structure; at the same conditions, a large-size channel is more easily to be deformed than a small one. The tapered-structure microchannels were also produced using a gray-scale mask. The result shows that a suitably low contrast for the photosensitive sacrificial material can lead to smooth and tapered microchannels.

Keywords: microchannel, polynorbornene, photolithography, thermal decomposition, contrast

* To whom correspondences should be addressed.

INTRODUCTION

Microfluidic devices have tremendous potential for applications in a variety of fields including drug discovery, biomedical testing, and chemical synthesis and analysis. In such devices, liquids and gases are manipulated in microchannels with cross-sectional dimensions on the order of tens to hundreds of microns. Processing in such microchannel devices offers a number of advantages including low reagent and analyte consumption, highly compact and portable systems, fast processing times, and the potential for disposable systems.¹⁻³ However, in spite of all of their promise, microfluidic devices are currently being used in a limited number of applications and are in general still rather simple devices in terms of their operational complexity and capabilities. For example, in terms of making truly portable microanalytical systems, one of the current difficulties involves the simple integration of electronic (e.g. sensing methods) and fluidic elements into the same device. One of the most important issues, which controls this ability to integrate functions into the same device and thus controls the level of functionality of a microfluidic device is the method used to fabricate the structure.

The two most prevalent methods for fabricating microfluidic devices to date involve either bonding together layers of ultraflat glass or elastomeric polymers such as poly(dimethylsiloxane).⁴ Both methods suffer from severe limitations and difficulties associated with integrating non-fluidic elements such as detectors with the microchannel system in the same substrate.⁴⁻⁶ A method developed recently, which uses microchannel fabrication methods that are completely compatible with standard silicon CMOS processes, can overcome many of these limitations and thus permit the integration of

electronic control, actuation, and detection systems into a single device during the same fabrication sequence.⁷ The first version of this method involves the use of a sacrificial polymer (polynorbornene) as a structural place-holder for channel formation using a conventional semiconductor process flow. The sacrificial polymer is first deposited as a blanket film by spin-casting or other deposition methods. A protective etch hard mask such as silicon dioxide is then coated onto the polymer layer and patterned using conventional photolithography and oxygen plasma etching. This patterned hard mask protects the underlying polymer from the etchant, leaving behind polymer relief patterns. These polymer structures are overcoated with a permanent structural material such as a polyimide or oxide. This sequence can be repeated to build up multilayer channel structures. Once all of the desired structures are formed, the entire device is heated to the decomposition temperature of the sacrificial polymer, leaving behind open microchannel structures.

This first sacrificial polymer fabrication method suffers from several limitations including the fact that it requires on the order of ten processing steps to complete the sequence for a single level of microchannels. Recently, an improved sacrificial polymer method using photodefinable norbornene copolymers was reported which completely eliminates the need for hard mask deposition, photoresist patterning, and plasma etching. This improved method thus dramatically reduces the number of process steps required, resulting in a process that can be completed in only five steps (see Figure 1).^{8, 9} In addition to significantly reducing the number of process steps required, this new method also opens up the possibility of forming arbitrarily shaped, three dimensional channel structures using gray scale lithography as suggested in our prior publication.⁹

These photosensitive norbornene copolymer sacrificial materials consist of formulations of copolymers of pendant butyl- and alkenyl-substituted norbornenes (PNB) with small additions of a photoinitiator (PI) to selectively induce crosslinking. The photolithographic characteristics, photoinitiation systems, and thermal decomposition properties of these sacrificial materials has been systematically investigated in previous studies.^{8,9} These experimental results provide the basic information required for the fabrication of microchannels using these sacrificial materials. However, it was shown in the work of Bhusrai, et al.⁷, that the cross sectional shape of channel structures produced using these sacrificial polymer methods may be arched under certain processing conditions. This unintentional curvature was ascribed to possible flow of the overcoat medium during the relatively high temperature decomposition process. However, no further information was available at the time however that could be used to guide process design to prevent this deformation in channel shape. The ability to prevent channel deformation is particularly important when the goal of the fabrication sequence is to build channels with controlled three dimensional cross sectional shapes.

The main goal of this work is to further develop and demonstrate the use of photodefinable sacrificial polymer fabrication methods to produce channel geometries with arbitrarily shaped cross-sectional profiles. This ability to control the shape of the channel cross-section is expected to be particularly useful in precisely controlling the flow of fluids in microchannel systems. The ability to control fluid flow patterns and dispersion by controlling the channel cross section is investigated in this work through computational fluid dynamics simulations. It was found that tapered cross sectional channel profiles are useful in preserving "plug flow" conditions in curved microchannels

and thus reducing dispersion of components in the flow. Therefore, the thermal decomposition of the photodefinable sacrificial polymers was studied in detail and novel heating protocols were developed that maintain the channel shape during decomposition. The use of these methods is finally demonstrated using grey scale lithography to produce microchannels with tapered cross sections.

SIMULATION OF FLOW IN CURVED CHANNELS

When designing and fabricating microfluidic devices, it is almost inevitable that channels with curved shapes will be required. For example, when designing a long separation column on a chip, turning the channel into a meandering path may be required to keep the device within some required size limits. In such cases, it can be extremely important to precisely control the fluid flow pattern in the channel so as to minimize differences in the residence time distribution of fluid traveling through the channel. In other words, one generally would like to maintain near "plug flow" conditions in devices used for separations, analysis, and other fluidic operations to prevent mixing and loss of spatial confinement of fluid samples after injection or separation. One particular problem is minimizing residence time variations for fluids traveling through corners and curved sections of microfluidic channels. In order to illustrate this point and investigate the improvements that could be realized by using channels with tapered cross sections, a series of computational fluid dynamics simulations were performed.

Fluent, a computational fluid dynamics (CFD) simulation package produced by Fluent Inc., was used to simulate the flow in a series of different corner designs for microchannels. GAMBIT, a preprocessor accessory for FLUENT made by Fluent Inc.,

was used to construct the desired model geometry, apply the meshing points to the model, and define the required boundary zones. Once defined, Fluent was used to simulate the flow pattern in each microchannel and to produce numerical and graphical results for each case.

In this work, a series of 90 degree turns in microchannels were simulated with varying cross sectional geometries. Figure 2 shows the cross sections of the four simulated channels. Fig. 2a shows the dimensions of a uniform area channel. Figures 2 b and 2c show channels with tapered corners. The taper improved the flow around corners with 2c representing a near optimized design. The inside radius of the turns was held constant at 60 μm and the outside radius of the turns was held constant at 120 μm . The same boundary conditions were applied in simulating the flow through these channels and a constant pressure outlet condition which was assumed to be atmospheric pressure. In this case, water was used as the flow media, but the results should be general to any Newtonian fluid under laminar flow conditions. Under these conditions, the flow rates and Reynolds numbers are quite low which indicates laminar flow conditions, and thus a laminar flow model was used in Fluent for solution of these problems. In order to look at the dispersion which would occur in fluid flowing around each of these microchannel corners, fluid packet trajectories and transit times around each turn were calculated. Figure 3 shows plots of the transit times for fluid packets as a function of radial distance along the corner for each type of turn structure. The appearance of different lines of packet transit times on these plots are due to the fact that fluid packets at different vertical positions within the channels also experience slight dispersion due to low velocities near the top and bottom surfaces of the channel.

Figure 3A clearly shows that the standard rectangular channel geometry would result in severe dispersion of an initially flat concentration profile after traveling around the 90 degree turn. Under laminar flow conditions, the relatively uniform velocity profile across the channel cross section coupled with the longer path length for fluid at the outside of the turn result in transit times which are a factor of 3 to 5 larger for fluid at the outside radius as compared to fluid at the inside radius. This dispersion would be even more greatly exaggerated for the case of a 180 degree bend. One natural solution to this problem is to decrease the velocity of the fluid near the inside radius of the turn in order to achieve equal transit times for the fluid irrespective of radial position. One way to achieve this velocity modification is to alter the cross sectional area of different regions of the channel. Figure 3B shows the transit time profile for fluid flowing around a turn in a triangular cross section channel. The reduced channel height at the inside radius of the turn would be expected to slow the velocity of fluid along the inside of the turn. Indeed, Figure 3B shows that the triangular cross section overcompensates and results in longer transit times for fluid near the inside radius as compared to fluid near the outside radius. From close inspection of the Fluent results, it is also apparent that channel sections which have two walls intersecting at acute angles leads to significant dispersion in these regions, and thus acute angles in the channel cross section geometry should be avoided if possible. Based on these facts, a series of rough optimizations were performed to design an improved channel cross section profile that would result in minimal dispersion around the simulated turn. Figure 3C shows the fluid transit time results for such an improved channel structure. The transit time profile is essentially uniform for fluid flowing around a 90 degree corner using this improved shape. Thus, it is clear that by engineering the

cross-sectional shape of microchannels in turns it should be possible to minimize dispersion in the flow profiles.

EXPERIMENTAL

The sacrificial polymer used in this work, which consists of the copolymer of butyl norbornene (BuNB) and alkenyl norbornene (ANB) in the molar ratio 73/27, was synthesized and supplied by Promerus LLC (Brecksville, OH). The polymer weight average molecular weight (M_w) and polydispersity index (PDI) were measured to be 425,000 and 3.74 respectively by gel permeation chromatography using polystyrene calibration standards. Bis(2,4,6-trimethylbenzoyl)-phenylphosphineoxide (Irgacure 819, Ciba Specialty Chemicals Inc.) was used as a PI for this work. Solutions of polynorbornene (PNB) and PI were prepared using mesitylene (MS, 97%, Aldrich) as the solvent. Two different formulations, PNB/PI/MS in a mole ratio of 16/0.32/84 (2 wt% initiator relative to dry polymer) and PNB/PI/MS in a mole ratio of 16/0.64/84 (4 wt% initiator relative to dry polymer) (weight ratios), were used in the experiments. After exposure and baking, polymer patterns were developed using xylene (98.5+%, Aldrich).

Thermal decomposition characteristics of the sacrificial polymer were investigated using a Seiko Instruments Inc. TG/DTA 320 system. Thermogravimetric analysis (TGA) measurements were performed under N_2 at a purge rate of 28 ml/min. The encapsulated sacrificial polymer structures were thermally decomposed in a Lindberg tube furnace purged with N_2 .

For microchannel fabrication, PNB/PI films were cast onto silicon wafers using a Brewer Science CEE 100 spinner and hotplate system. A 3.5 ~ 4.0 μm thick PNB/PI film

was obtained at a spin speed of 2400 rpm and a softbake of 110°C for 60 seconds. Film thicknesses were measured using a Veeco Dektak profilometer. An OAI Mask Aligner equipped with an *i*-line filtered UV irradiation source (365 nm wavelength) was used to expose and pattern the PNB/PI films. Before exposure, the intensity of UV light source was measured using an OAI Model 356 Exposure Analyzer with a 365 nm probe. After exposure, samples were post-exposure baked at 120°C for 30 minutes in an oven. Samples were developed using a continuous spray of xylene while the wafer was spun at 500 rpm.

Removal of any polymer residue from the developed patterns was accomplished using a PlasmaTherm reactive ion etching (RIE) system using the following conditions: 5 sccm CHF₃, 45 sccm O₂, 250 mTorr, 300 W, 35°C. The etching rate of the polymer under these conditions is approximately 300 nm/min. Plasma enhanced chemical vapor deposition (PECVD) was performed to deposit an SiO₂ overcoat for encapsulation of the polymer channel patterns. The SiO₂ was deposited with a PlasmaTherm PECVD using the following conditions: 380 kHz RF frequency, 50W power, 200°C, 550mTorr, and a gas mixture of N₂O (1400 sccm) and 2% SiH₄ diluted in N₂ (400 sccm). The deposition rate for the oxide using these conditions is approximately 50 nm/min.

Thermal Decomposition Program

For the thermal decomposition process, the fractional decomposition can be calculated from the TG curve as shown in equation (1):

$$\alpha = \frac{W_0 - W}{W_0 - W_f} \quad (1)$$

where W_0 is the initial mass, W is the mass remaining at some time during the decomposition, and W_f is the final mass of the sample at the end of the thermal cycle. The kinetic description for thermal decomposition of the polymer is generally expressed as shown in equation (2):

$$\frac{d\alpha}{dt} = k(1-\alpha)^n = A \exp\left(-\frac{E_a}{RT}\right)(1-\alpha)^n \quad (2)$$

where n is the overall order of decomposition reaction, A is the Arrhenius pre-exponential factor, and E_a is the activation energy of the decomposition reaction.

In order to avoid a sudden and large release of the gaseous decomposition products from the polymer patterns that may result in distortion of the channel structure, it is desired to keep the decomposition rate $\left(\frac{d\alpha}{dt}\right)$ constant during the entire decomposition process. Assuming the decomposition rate is equal to a constant, r , throughout the decomposition process then:

$$\frac{d\alpha}{dt} = r, \text{ and, } t = 0, \alpha = 0 \quad (3)$$

Integrating equation (3) gives the general desired result shown in equation (4):

$$\alpha = rt \quad (4)$$

Assuming that the reaction order, activation energy, and pre-exponential factor do not change significantly during the decomposition, $\frac{d\alpha}{dt}$ and α can be replaced with r and rt respectively in equation (2) which results in the following equation:

$$r = A \exp\left(-\frac{E_a}{RT}\right)(1-rt)^n \quad (5)$$

It is now possible to rearrange equation (5) to solve for the necessary temperature versus time profile that is required to maintain a constant rate of polymer decomposition throughout the entire process. The explicit expression for temperature versus time is shown in equation (6).

$$T = \frac{E_a}{R} \left[\ln \frac{A(1-rt)^n}{r} \right]^{-1} \quad (6)$$

Thus, in order to design a heating profile it is necessary to specify only four parameters: the three kinetic parameters (A , E_a and n) that describe the polymer decomposition, and r the desired polymer decomposition rate. Based on regression of TGA data performed in previous experiments⁹, the kinetic parameters for the polymer used in this work were determined to be: $A = 5.835 \times 10^{14} \text{ min}^{-1}$, $E_a = 207 \text{ kJ/mol}$ and $n = 1.05$. Thus, for a given constant decomposition rate, r , one can obtain a curve of temperature versus decomposition time.

RESULTS AND DISCUSSIONS

Decomposition Condition: Thermal decomposition of the sacrificial polymer was performed in a pure nitrogen atmosphere in order to avoid any oxidation of the polymer that could result in the formation of non-volatile decomposition products and undesirable residue in the microchannels. In addition to using an inert atmosphere, as suggested previously a controlled heating profile was used to maintain a relatively constant polymer decomposition rate. This constant decomposition rate ensures that gaseous products are not released so quickly that pressures high enough to significantly deform the channel shape are generated.

Figure 4 shows curves of the decomposition rate versus time for pure PNB samples decomposed at both a constant temperature of 425°C (isothermal decomposition) and various heating rates (dynamic decomposition) respectively. In each case, there is a peak in the decomposition rate. The width of the peak corresponds to the transition period during the conversion of sacrificial polymer to gaseous products. Higher heating rates or high temperature isothermal decompositions result in a sharp peak in the decomposition rate profile. This implies that the majority of the decomposition process occurs over a short time interval, thus resulting in a sudden and large release of the gaseous decomposition products. It was therefore expected that controlling the decomposition rate at a constant low level using controlled heating profiles could eliminate this phenomena and thus prevent channel distortion during decomposition. It was decided to test this theory by comparing the effect of various decomposition procedures on the final resulting microchannel shapes and sizes.

Based on equation (6), the temperature versus time heating profiles required to achieve decomposition rates of 1, 2 and 3 %/minute were calculated and are shown in Figure 5. The figure illustrates that, at a constant decomposition rate, the decomposition temperature during most of decomposition time should be set relatively low with a slight ramp rate. However as the decomposition nears completion, higher temperatures can be used which helps obtain complete decomposition of the polymer within a reasonable time scale.

In order to preclude the need for complex temperature controllers for the decomposition furnaces used in the microchannel fabrication process, representative temperature profiles that closely approximate the smooth temperature versus time curves

produced using equation (6) were used. Figure 6 shows the temperature versus time curve calculated using equation (6) and the corresponding simple mimic heating profile that was tested in the Lindberg decomposition furnaces for device fabrication. Figure 7 shows TGA results for the simple mimic heating program that was designed to achieve a 1%/minute decomposition rate. The DTG curve demonstrates that the decomposition rate does indeed fluctuate closely around the desired 1%/minute level without extreme variations. Thus, the sharp peak in the decomposition rate shown in Figure 4 can be avoided by using more intelligent heating profiles. When this same mimic heating profile is used in processing encapsulated polymer samples, no distortion in the encapsulated channels was observed but electron microscopy revealed that small amounts of polymer residue were left in the channel structures. Two different modifications to the mimic heating profile were tested in an attempt to remove this residual polymer. In the first case, a final hold at 455°C for one hour was used in an attempt to remove the residual polymer. This high temperature hold did indeed reduce the residual remaining polymer substantially as observed in SEM cross sections, but some remaining residue was left even after the one hour hold. A second method which involved doubling the intermediate holds shown in Figure 6 was also tested. This effectively reduced the average decomposition rate even further to somewhere approaching the 0.5%/minute level. In this case, it was observed that no distortion of the channel profile occurred during the decomposition and essentially no polymer residue was found in the microchannel after decomposition. This suggests that there may be additional byproducts formed during the decomposition if the process is ramped too quickly which result in a residue that can be difficult to remove with even high temperature processing. Longer holds at lower

temperatures can be used to both slow the decomposition rate and thus reduce pattern profile distortion and to eliminate residual polymer in the final channel structures.

Microchannels encapsulated with polyimide and SiO₂: Microchannels have been made following the scheme in Figure 1. In the processing, a 3.5 ~ 4.0 μm thick PNB/PI film (4 wt% initiator in PNB) was cast using a spin speed of 2400 rpm and softbake condition of 110°C/60 seconds. The film was exposed to UV light using a chrome on quartz mask with dose of 450 mJ/cm² and post-exposure baked at 120°C for 30 minutes in an oven. After post-exposure baking, the film was spray developed using xylene to produce the desired channel patterns. There was no noticeable residue remaining after development in the patterned areas, but direct overcoating of the encapsulant material on the as-developed features resulted in poor adhesion to the substrate. In fact, small bubbles were observed to form in the overcoat materials in the areas where the sacrificial polymer was presumably developed cleanly away from the substrate. Therefore, it was concluded that there must be some small amount of remaining polymer residue after development that prevents good adhesion of the overcoat to the substrate. In order to avoid this phenomenon, a residue removal treatment was employed by dry etching in an oxygen plasma using an RIE before the channel patterns are encapsulated. After residue removal using the plasma, samples were then encapsulated using either polyimide or SiO₂. Polyimides are good materials for encapsulation because they display high glass transition temperatures and thermal stability, low dielectric constant, modulus, moisture adsorption and stress⁷. In this work, HD Microsystems PI 2734 polyimide, was used to overcoat some of the channel structures. In these cases, the PI 2734 was spin-coated on

the top of the channel patterns at a speed of 2300 rpm for 30 sec, and cured at 350°C for 1 hr under N₂. The thickness of the polyimide layer under these conditions is approximately 4.5 μm. In addition, some channel structures were encapsulated using SiO₂. In these cases, a 2 μm thick encapsulation layer of SiO₂ was deposited using the PECVD recipe described earlier.

The decomposition of the encapsulated polymer patterns was performed at various decomposition rates to investigate the effect of the rate on the channel structure. Figures 8a through 8g show SEM images of the channel encapsulated with polyimide and decomposed at different rates using different heating profiles. The results indicate that the decomposition rate does indeed affect the channel structure significantly. At low decomposition rates (1 or 2%/minute), the channel structures produced maintain the size and shape of the original PNB sacrificial polymer pattern. However, at relatively high decomposition rates (3%/min) or when a high constant temperature decomposition process is used, the microchannels are distorted into dome or arc shaped profiles. It is also obvious that this distortion problem becomes a more important issue for microchannels as their lateral size increases. Channels with larger widths clearly deformed more than channels of smaller dimensions. SEM images of channels encapsulated with SiO₂ are shown in Figures 9a to 9f. It was observed that the extent of channel deformation appears to be higher in the SiO₂ overcoated structures as compared to the polyimide overcoated channels at the same nominal channel feature sizes and polymer decomposition rates. This larger deformation in the SiO₂ overcoated samples could be due to both differences in the mechanical properties of the two overcoat

materials and differences in the diffusion rate of the decomposition products through the overcoat materials.

Microchannels with tapered cross-section structure: As discussed previously, one of the goals of this work was to provide a simple fabrication method for microchannels with tapered cross sectional profiles that could be used to control fluid flow patterns in microchannels. In order to fabricate the tapered microchannel structures, the concept described here is to use a gray-scale lithography process employing a gray-scale photomask and a low contrast photosensitive sacrificial material. A series of experiments were performed to investigate the possibility of using such an approach for producing microchannels that are shaped in a controlled manner in all three dimensions.

On the mask used in these experiments, channel features were designed with an approximately linear gradient in percent transmission, which were made by patterning various regions or "zones" across the width of the channel with varying ratios of chrome stripes to clear transparent area. In this particular case, the chrome stripe features were designed to be 200 nm in size and thus served as sub-resolution features for the photosensitive sacrificial polymers used in this work. The masks were fabricated from these designs by electron beam lithography at ETEC Systems (Hayward, CA). Table 1 describes the two main channel features used in this work in more detail. Using this type of gray-scale mask allows for the photosensitive sacrificial material to be exposed to a range of doses across the width of the channel feature using a single lithographic exposure step. This exposure gradient in conjunction with a low contrast resist material can be used to produce a feature that is shaped in both the lateral and vertical directions

with respect to the plane of the substrate in a single lithographic process. Two photosensitive materials with different contrast levels were used to generate tapered microchannel structures with this mask. Figure 10 shows the contrast curves for the two photosensitive sacrificial polymer formulations used in this work. The methods of measuring contrast curves and calculating contrast values for these materials have been discussed previously in the literature.^{8,9} The contrast factors for these two systems are a modest 0.51 and 0.85 for the 2wt% (referred to as material 1) and 4wt% (referred to as material 2) photoinitiator relative to dry polymer loadings respectively.

Using this contrast curve data, it is possible to quickly calculate a rough prediction of the pattern profile that will result from exposure using a gray-scale mask with these photosensitive materials if the relative transparency as a function of position on the mask is known accurately. Based on polynomial fitting, the contrast curves can be adequately described using the following functions:

$$f_1 = 0.0236[\log(D)]^3 - 0.357[\log(D)]^2 + 1.8185[\log(D)] - 2.127 \quad (7)$$

$$f_2 = 0.0352[\log(D)]^3 - 0.6526[\log(D)]^2 + 2.9467[\log(D)] - 2.921 \quad (8)$$

Here f_i is the fraction of the film thickness remaining after exposure to a dose D and wet development for material i .

An approximate shape of the channel patterns that will be produced from a gray-scale mask can thus be predicted using Eq. 9.,

$$d(x) = f_i(\log[D \cdot TP(x)]) \cdot FT, \quad (9)$$

where, f_i is the contrast function for material i , $d(x)$ is the thickness of the film (after development) at a certain position x across the channel pattern, $TP(x)$ is the fractional transparency of the mask at the position x across the feature, D is the nominal exposure dose used, and FT is the original thickness of the cast film. The outline of the simulated channel pattern consists of the points calculated by Eq. 9, which were then smoothed by seven-point smoothing, Eq. 10.

$$S_i = \frac{Y_{i-3} + 2Y_{i-2} + 3Y_{i-1} + 4Y_i + 3Y_{i+1} + 2Y_{i+2} + Y_{i+3}}{16} \quad (10)$$

where S_i and Y_i are the smoothed signal and original signal for the i^{th} point respectively.

Tapered-structure channel patterns were fabricated using the gray-scale lithographic approach using a sequence of steps similar to those outlined in Figure 1. First, 12 μm thick PNB/PI films were cast using a spin speed of 700 rpm and softbake condition of 110°C for 2 minutes. The films were then exposed to UV light with the gray-scale mask. The nominal exposure dose was set using the contrast curve data for the photosensitive material to obtain a film with 80% original thickness remaining after development under a 100% transparent feature. The doses used were 1300 mJ/cm^2 and 165 mJ/cm^2 for 2 wt% and 4 wt% initiator loadings respectively. The films were post-exposure baked at 120°C for 30 minutes in oven. The films were spray developed using xylene at a spin speed of 500rpm for 30 seconds. The final shape of the microchannel patterns was measured using profilometry.

Figures 11 and 12 show the real Feature I type PNB patterns produced as measured by profilometry, and for comparison the predicted microchannel patterns (using equations 7 through 10), for the systems with 2 wt% and 4 wt% initiator loadings. A comparison between different patterns produced by the two photosensitive materials clearly shows that the material with the lower contrast produces a profile that more closely resembles the desired smoothly tapered structure. However, it can be seen that the simple prediction of the profile shape only roughly approximates the actual feature produced using this method. Upon closer inspection of the mask, it was apparent that the desired smooth gradient in transmission was not faithfully reproduced into the mask due to the extremely small feature sizes used for the constituent patterns. This brings up the issue that accurate gray scale mask production for such a method may in fact be a challenging task. In any case, with more careful attention and accurate transfer of the design to the mask, it should be possible to use the contrast data for a material in conjunction with equations (7) through (10) to design a gray-scale mask feature for a specific photosensitive material that can be used in principle to obtain any desired pattern shape.

The tapered polymer microchannel patterns were next overcoated and decomposed in order to test the ability to transfer the tapered profile into the final microchannel. First, any polymer residue was removed from the substrate using an oxygen RIE plasma etch. The channel patterns were then encapsulated with SiO₂ using the same conditions described previously. The thermal decomposition of encapsulated channel patterns was performed under N₂ with a decomposition rate of 0.5%/minute. SEM images of the resulting tapered microchannels are shown in Figures 13a to 13d.

Due to the ability to carefully control the decomposition rate of the polymer by controlling the heating profile during decomposition, no deformation was observed in the channel structure. This can be seen by comparing the profiles of the original PNB patterns in Figures 11 and 12 with the SEM channel cross sections in Figure 13. The widths of the channels in Figure 13c and 13d are narrower than the feature sizes on the gray-scale mask due in part to slight RIE over-etching during the polymer residue removal step. Comparing figures 13a and 13b with figures 13c and 13d, it can be seen that a low contrast sacrificial material is desirable for the fabrication of smoothly tapered microchannel structures. As expected, the final shape of the channel structure is determined by a combination of the gray-scale pattern on the mask, the contrast of the photosensitive material, and the nominal exposure dose used in printing the feature.

In order to obtain an idea of the effectiveness of fabricated channel cross sections in reducing dispersion in flow around microchannel corners, the expected fluid transit times around a corner of the shape shown in Figure 11a were simulated using Fluent as described previously. Figure 14 shows the predicted transit times for flow around this corner using the boundary conditions and velocities used in the earlier idealized channel simulations. It is clear from this simulation that even the crudely shaped channel fabricated for demonstration purposes in this work would be expected to perform better than the standard rectangular cross section channel. Further, it is hoped that by optimizing mask design and process conditions, that a more ideal shape similar to that shown in Figure 3C can be achieved and used for device fabrication. This further refinement of the process is the subject of ongoing work.

CONCLUSIONS

The fabrication of microchannels has been demonstrated by using photosensitive sacrificial polymer materials. The process consists of patterning the sacrificial polymer via photolithography, removal of polymer residue using RIE, encapsulation with a dielectric medium, and thermal decomposition of encapsulated polymer channel patterns. A method for designing heating programs to keep the thermal decomposition of sacrificial polymer at a constant rate was presented using the kinetic model of polymer decomposition. Heating programs designed using this approach have been demonstrated to prevent sudden and large decomposition rates (i.e. which result in drastic release of gaseous decomposition products that distort channel features), and were also shown to produce microchannel patterns with well controlled shapes that do not exhibit any substantial deformation after the thermal decomposition of the sacrificial polymer. Controlling the decomposition rate and slowly releasing the gaseous decomposition products allows the decomposition products to permeate through the overcoat at a rate roughly equivalent to the decomposition rate, and thus avoids the build-up of large pressures in the microchannel which can lead to distortion and failure of the structure. It was also found that larger channels have a higher tendency toward distortion. A gray-scale lithographic process has been developed and demonstrated for the production of microchannels with tapered cross-sections. Such tapered channels have been shown through simulation to be able to reduce effects such as dispersion that are detrimental to microfluidic system performance.

ACKNOWLEDGEMENTS

The authors would like to gratefully acknowledge the financial support for this project from National Science Foundation (Grant #DMI-9980804). The authors would also like to thank ETEC Systems for fabrication of the gray scale photomasks used in this work.

REFERENCES

1. J. C. McDonald, D. C. Duffy, J. R. Anderson, D. T. Chiu, H. Wu, O. J. A. Schueller and G. M. Whitesides, **Electrophoresis**, 21, 27 (2000).
2. V. Dolnik, S. Liu and S. Jovanovich, **Electrophoresis**, 21, 41(2000).
3. M. Koch, A. Evans and A. Brunnschweiler, Microfluidic Technology and Applications, American Technical Publishers Ltd., Ch. 6 and 7, (2000).
4. N. F. Raley, J. C. Davidson and J. W. Balch, **Proc. SPIE**, 3224, 185(1997).
5. N. F. Raley, J. C. Davidson and J. W. Balch, **Proc. SPIE**, 2639, 40(1998).
6. P. Pethig, J. P. H. Burt, A. Parton, N. Rizvi, M. S. Talary, and J. A. Tame, **J. Micromech. Microeng.**, 8, 356 (1998).
7. D. Bhusari, H. Reed, M. Wedlake, A. Padovani, S. A. Bidstrup-Allen and P. Kohl, **IEEE J. Microelectromech. Systems**, 10, 400 (2001).
8. X. Q. Wu, H. A. Reed, L. F. Rhodes, E. Elce, R. Ravikiran, R. A. Shick, C. L. Henderson, S. A. Bidstrup Allen and P. A. Kohl, **J. Electrochem. Soc.** accepted.
9. X. Q. Wu, H. A. Reed, L. F. Rhodes, E. Elce, R. Ravikiran, R. A. Shick, C. L. Henderson, S. A. Bidstrup Allen and P. A. Kohl, **J. Appl. Polym. Sci.** in press.

Figure Captions

Figure 1. Schematic of processing steps for microchannel fabrication using photodefinable polymer sacrificial materials.

Figure 2. Schematic of microchannel cross sections simulated using Fluent.

Figure 3. Fluid transit time plots for flow around 90 degree turns with 60 micron inside radii for microchannel cross sections shown in Figure 2, (a) corresponds to Fig. 2a, (b) corresponds to Fig. 2b, and (c) corresponds to Fig. 2c.

Figure 4. Differential thermal gravimetric (DTG) curves for pure PNB samples decomposed at a constant temperature of 425°C (isothermal decomposition) or various heating rates (dynamic decomposition).

Figure 5. Calculated trends of temperature versus time for the decomposition of pure polymer at rates of 1, 2 and 3%/min.

Figure 6. Calculated and mimic heating programs for the decomposition of pure polymer at a rate of 1%/min.

Figure 7. TGA results for the mimic heating program set for a nominal decomposition rate of 1%/minute.

Figure 8. SEM images of the channels encapsulated with polyimide and decomposed with at rates of (a, b) 1%/minute, (c, d) 2%/minute, (e, f) 3%/minute, and (g) at a constant temperature of 425°C.

Figure 9. Microchannels encapsulated with SiO₂ and decomposed at rates of (a, b) 0.5, (c, d) 1, and (e, f) 3%/minute.

Figure 10. Contrast curves for photosensitive PNB formulations with various photoinitiator loadings: 2 and 4 wt% (in PNB).

Figure 11. Real and simulated channel patterns (with Feature I of the mask) for the system with 2 wt % initiator loading.

Figure 12. Real and simulated channel patterns (with Feature I of the mask) for the system with 4 wt % initiator loading.

Figure 13. SEM images of tapered microchannels made by using (a) Feature I of the gray scale mask with 2% PI, (b) Feature II with 2%PI, (c) Feature I with 4% PI, and (d) Feature II with 4% PI.

Figure 14. Fluent simulation of fluid transit times around 90 degree corner with 60 micron inside radius for microchannel with cross section similar to that shown in Figure 11a.

Table 1 Characteristics of the gray-scale microchannel photomask

Feature I

Channel Width	60 μm					
Zone Size:	6 μm	6 μm	6 μm	6 μm	6 μm 6 μm
Transparency (TP):	100%	90%	80%	30%	20% 10%

Feature II

Channel Width	80 μm					
Zone Size:	4 μm	4 μm	4 μm	4 μm	4 μm 4 μm
Transparency (TP):	100%	95%	90%	15%	10% 5%

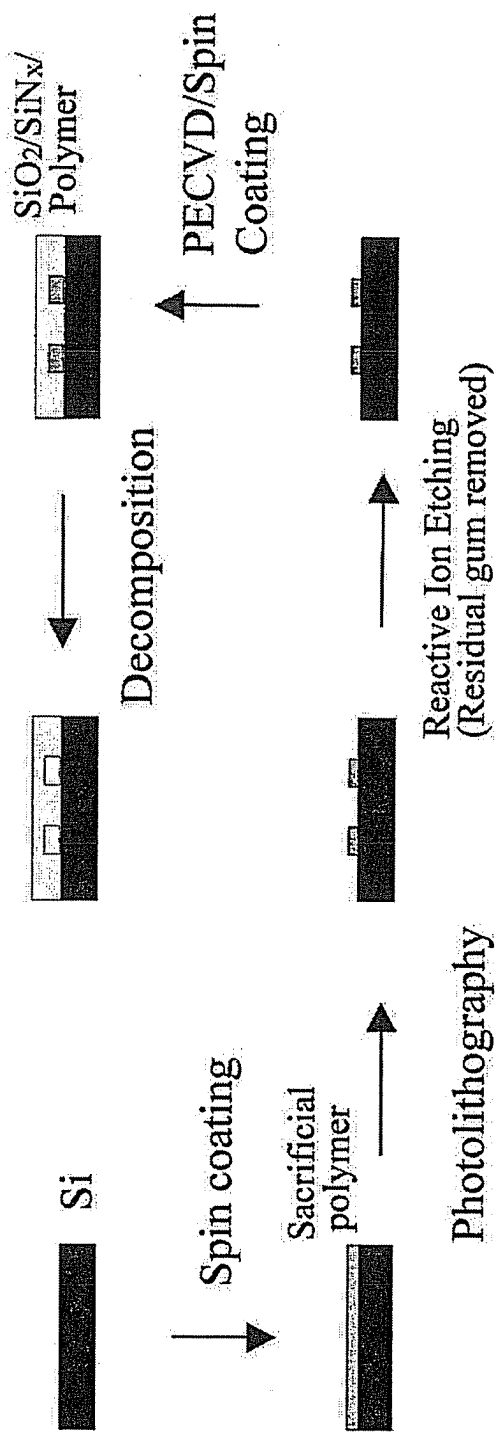
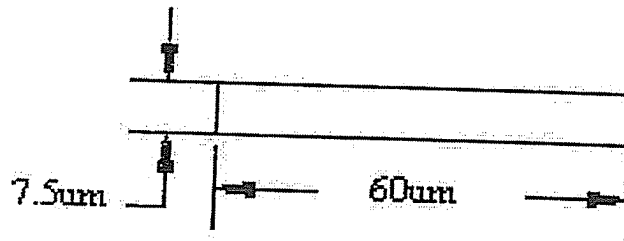
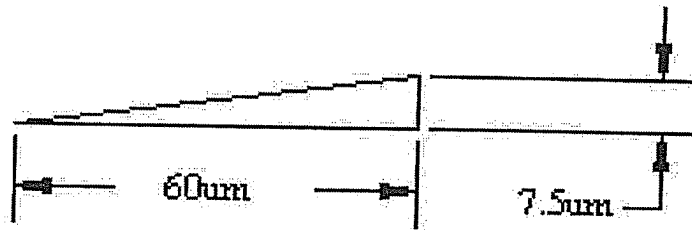


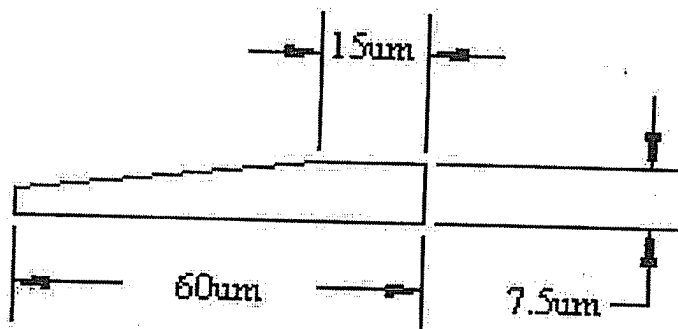
Figure 1



A. Rectangular Corner



B. Triangular Corner



C. Best Simulated Corner

Figure 2

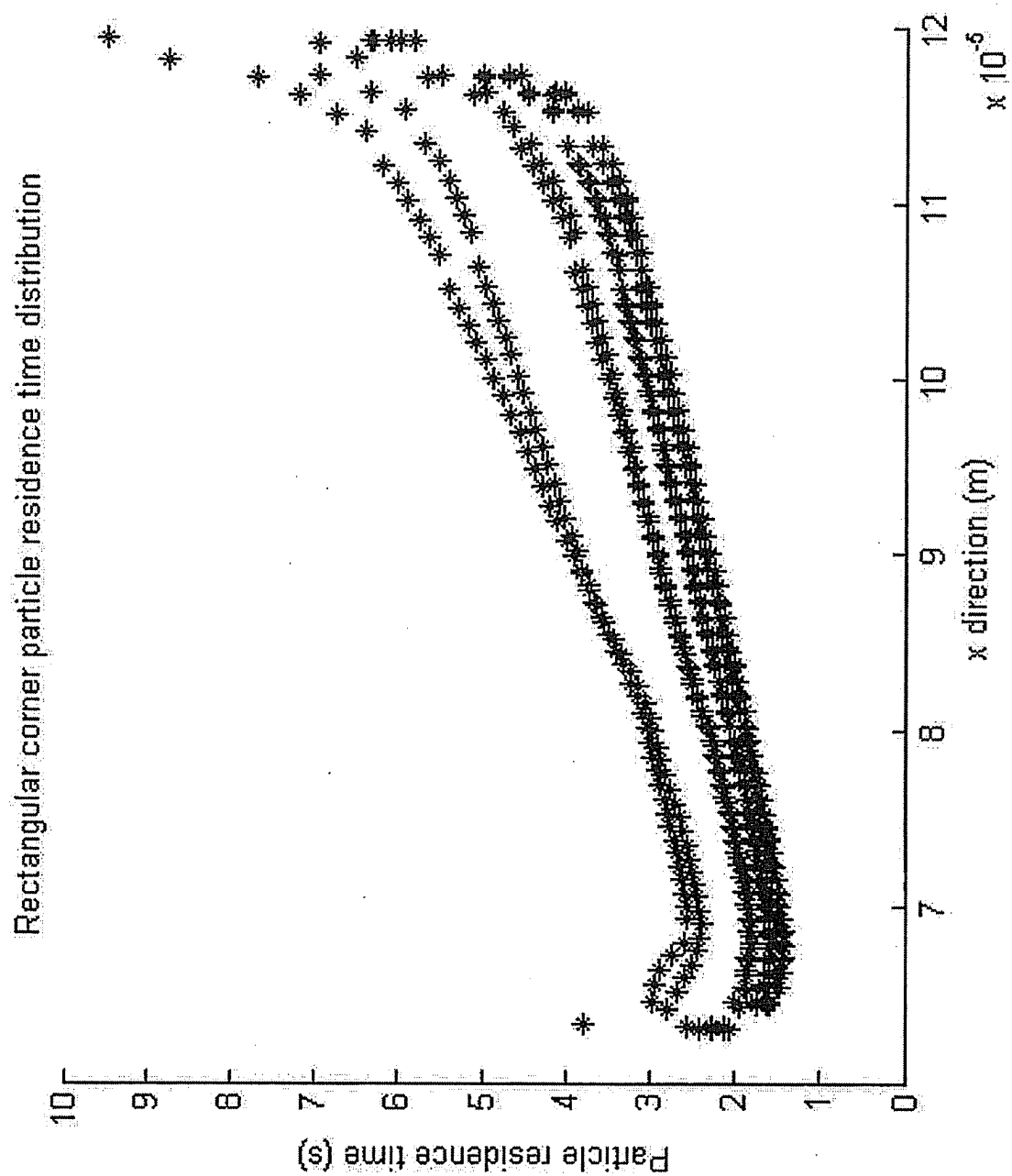


Figure 3A

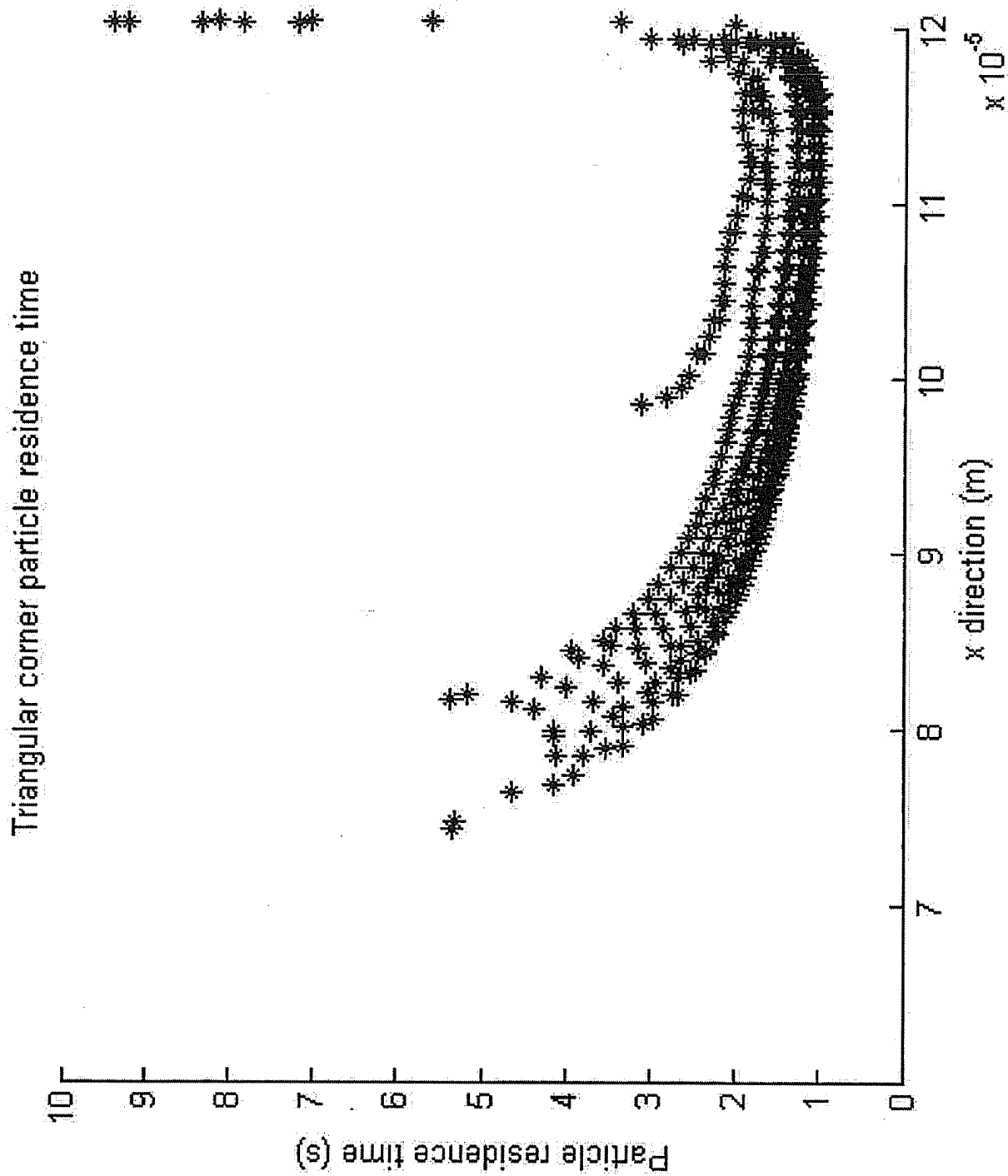


Figure 3B

Best simulated corner design

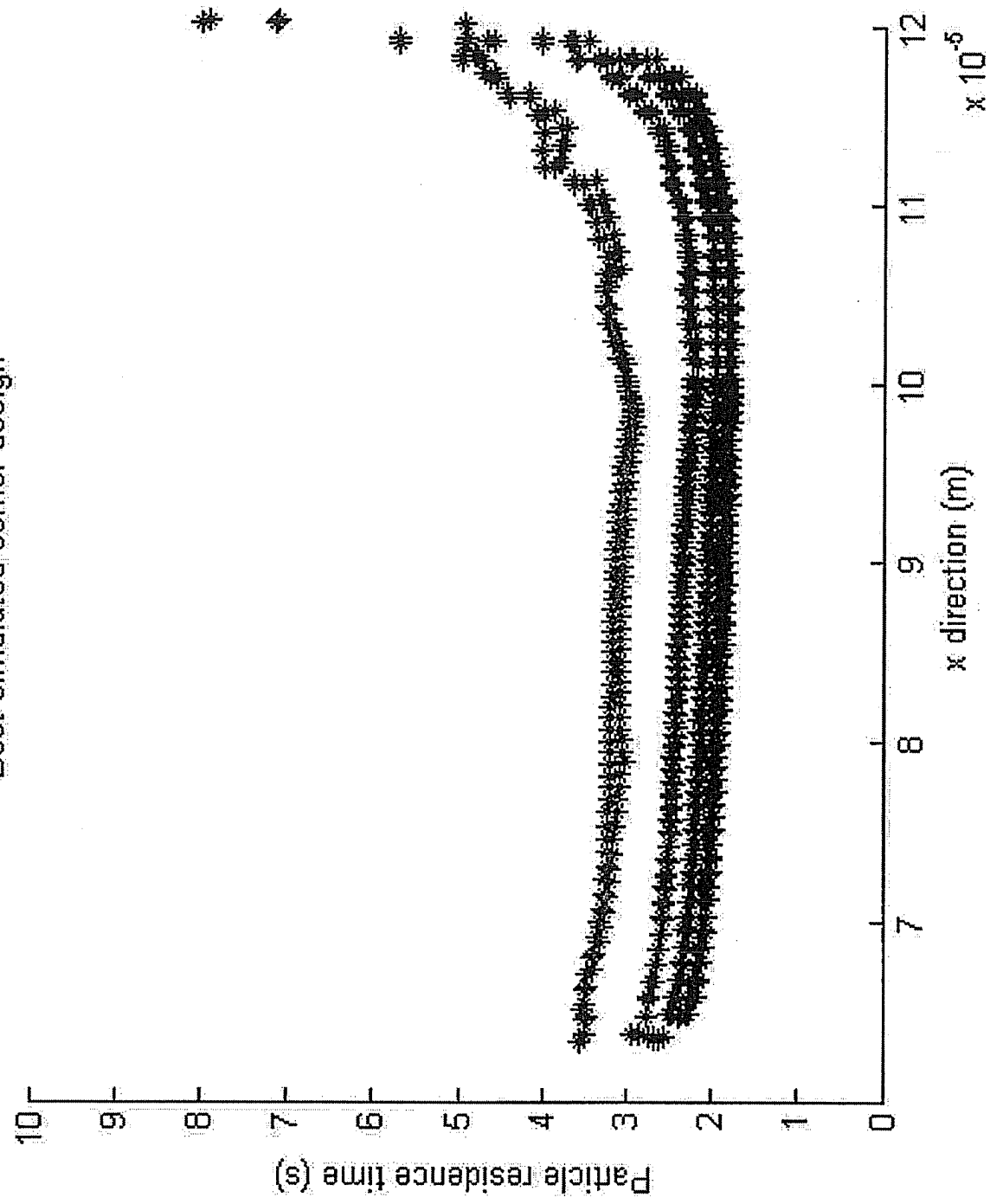


Figure 3C

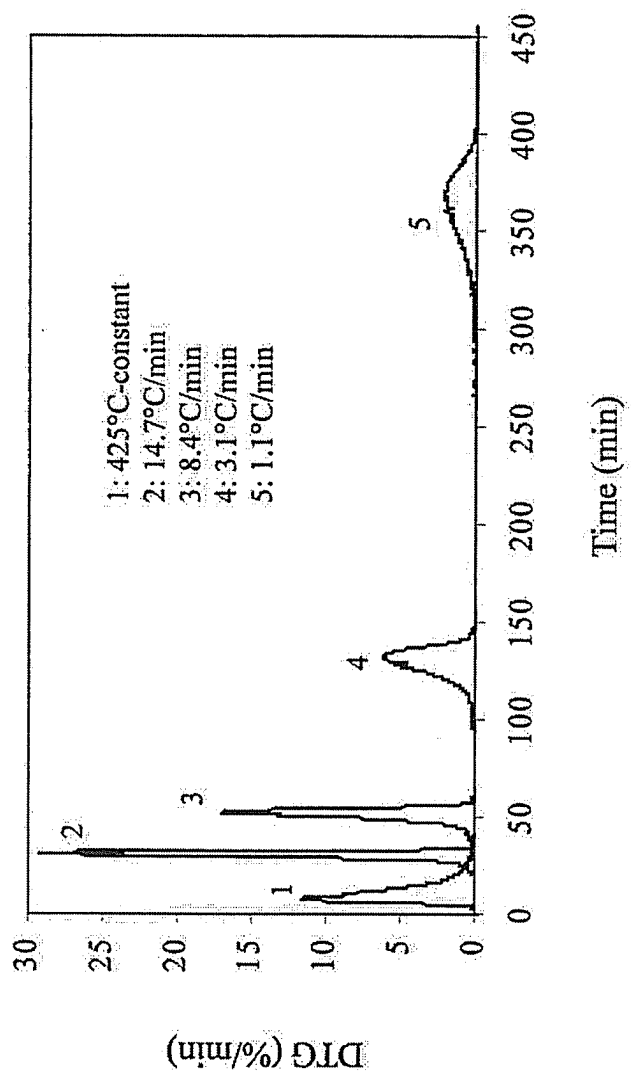


Figure 4

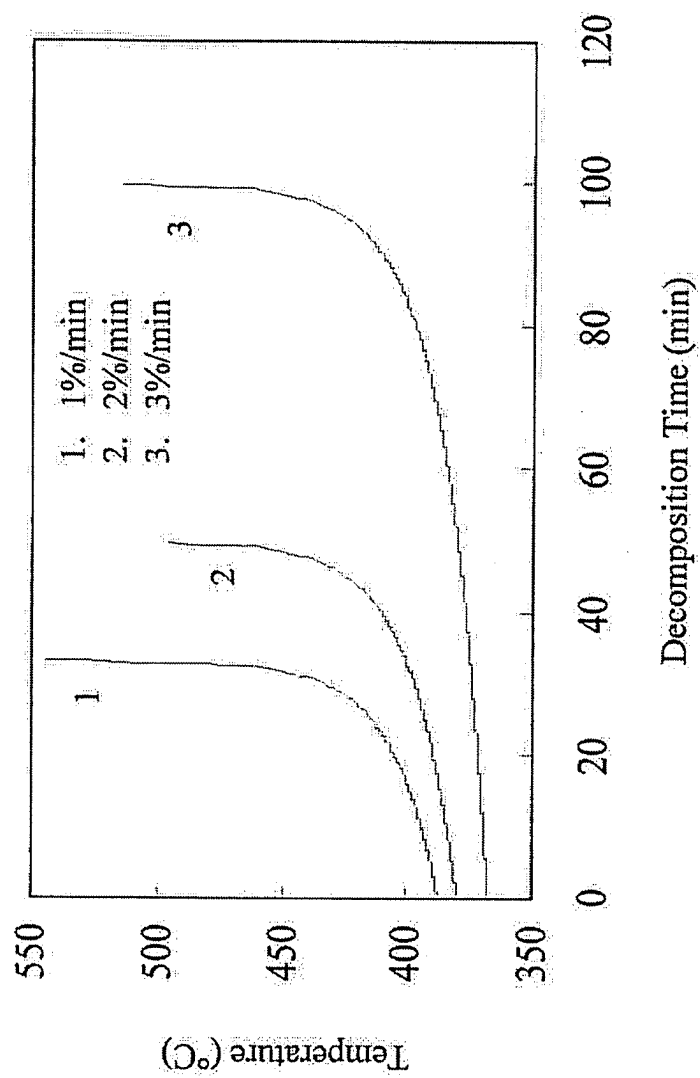


Figure 5

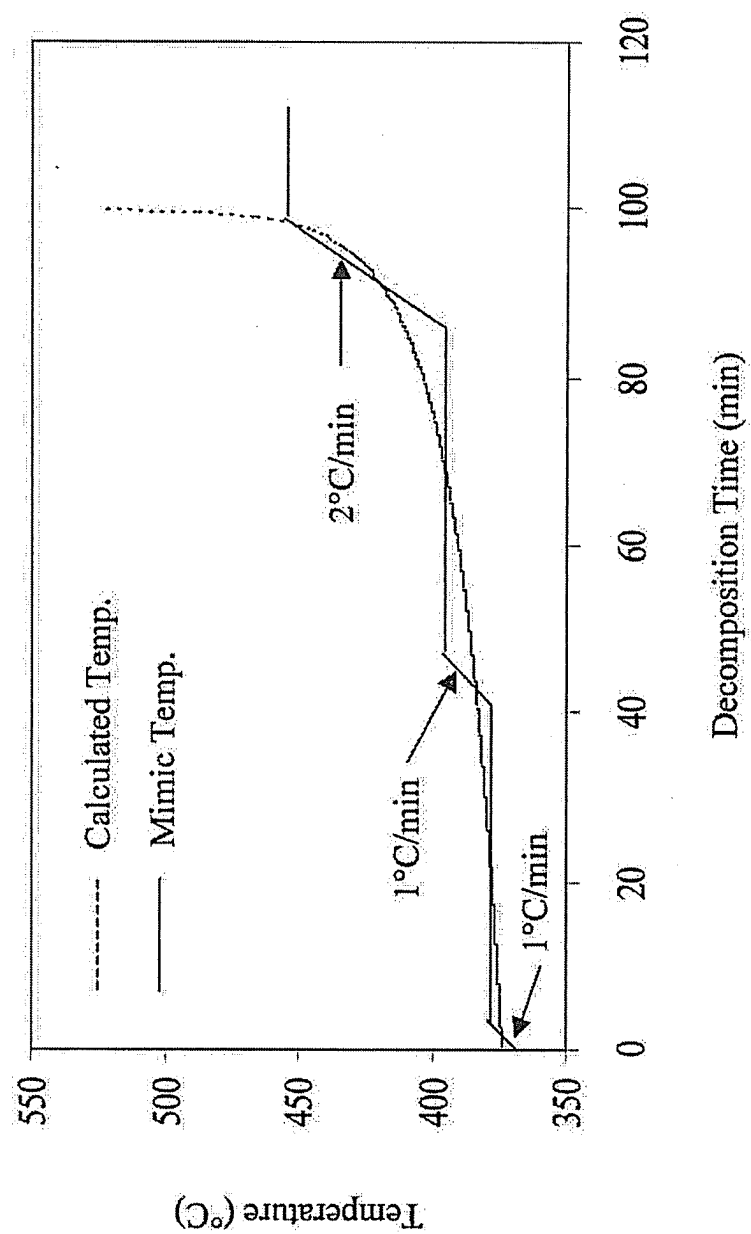


Figure 6

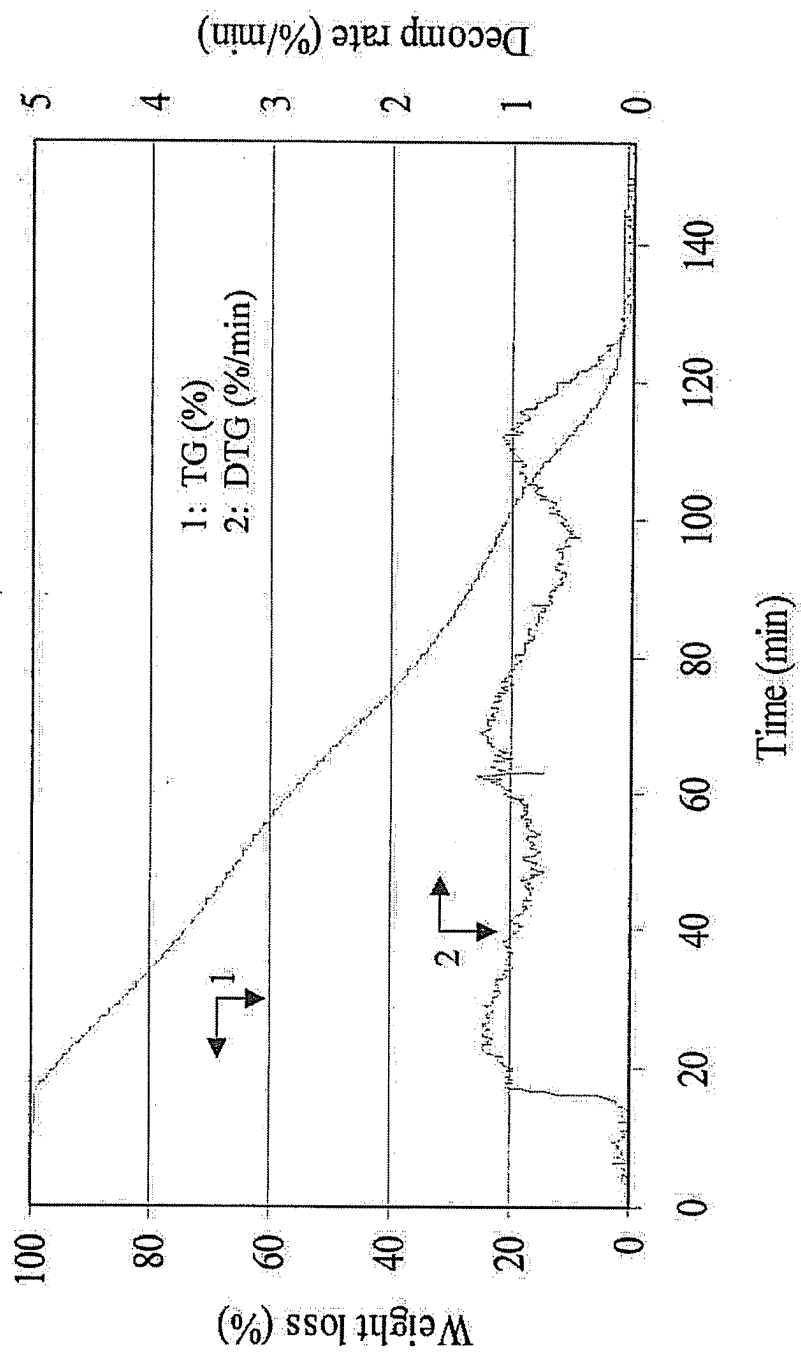


Figure 7

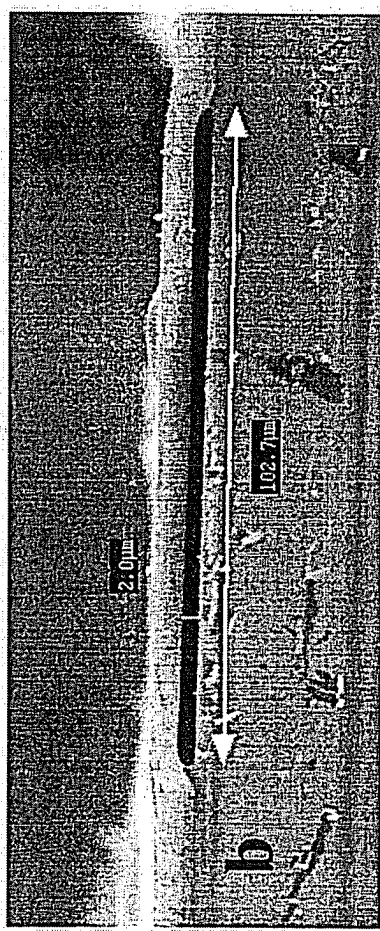


Figure 8

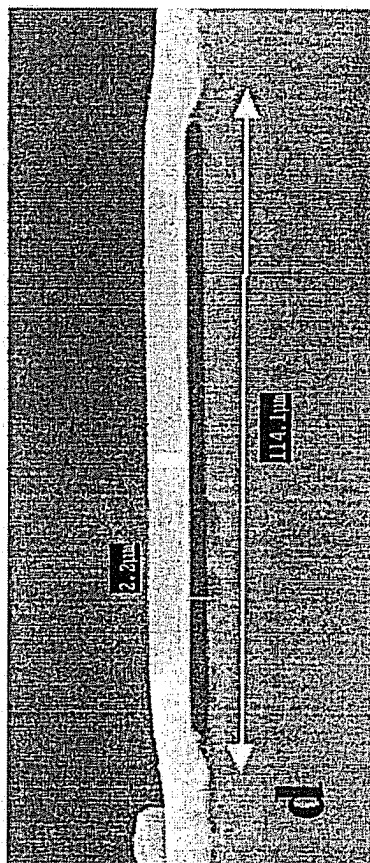
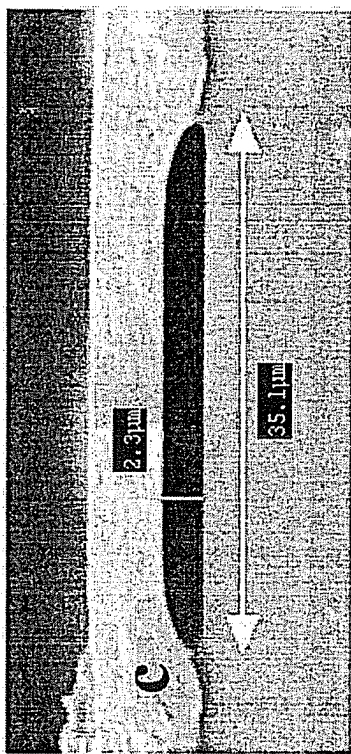


Figure 8

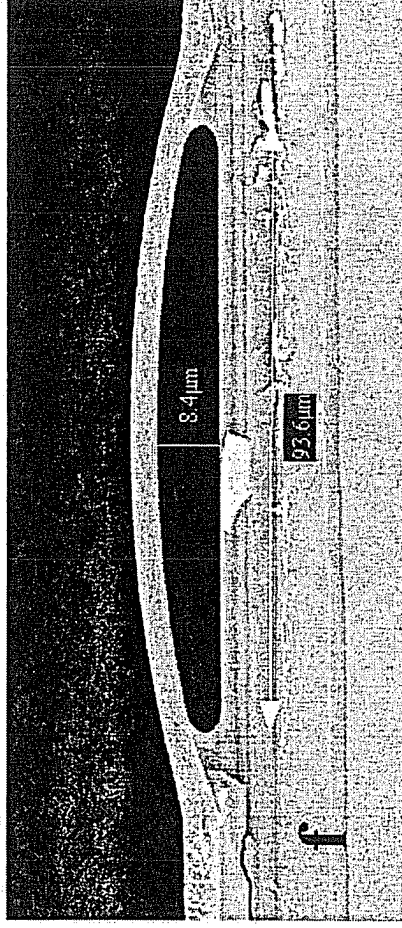
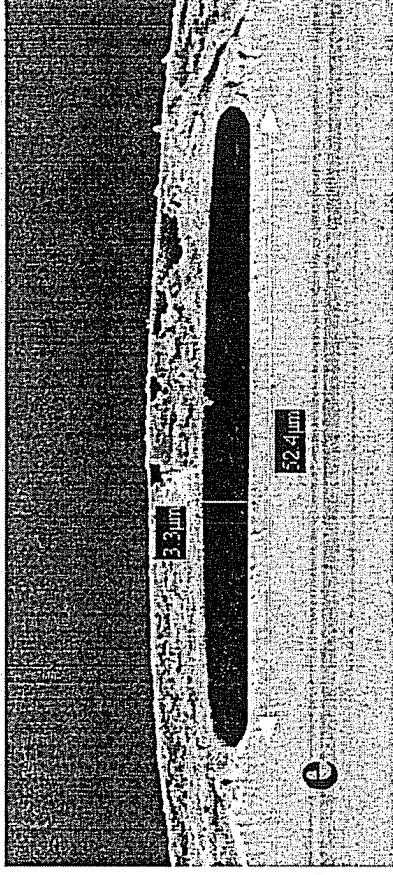


Figure 8

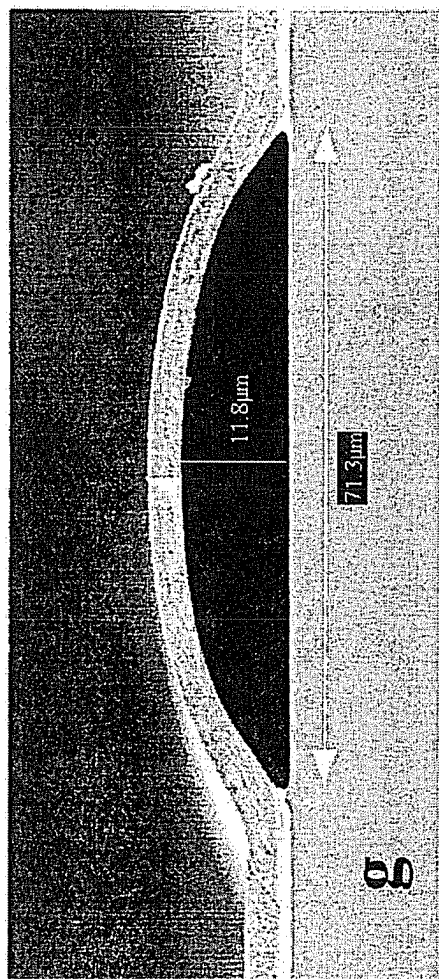


Figure 8

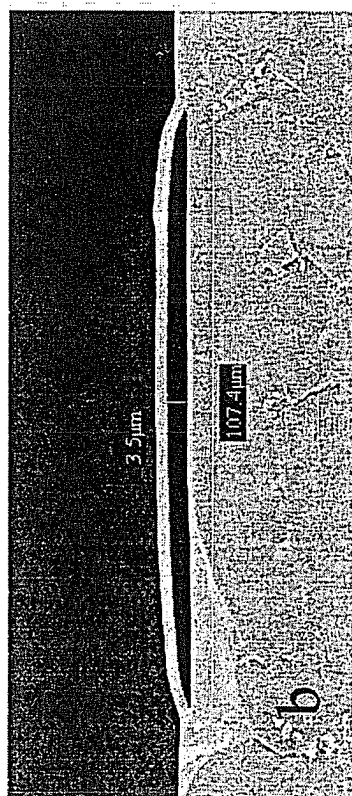
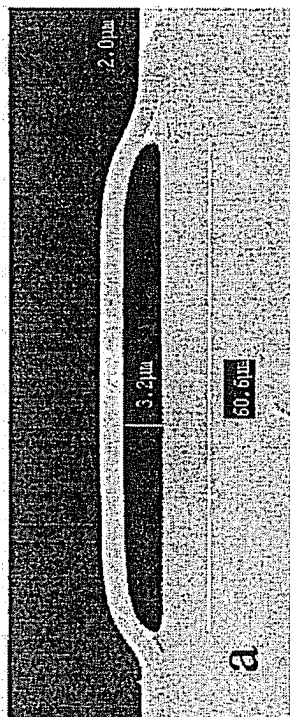


Figure 9

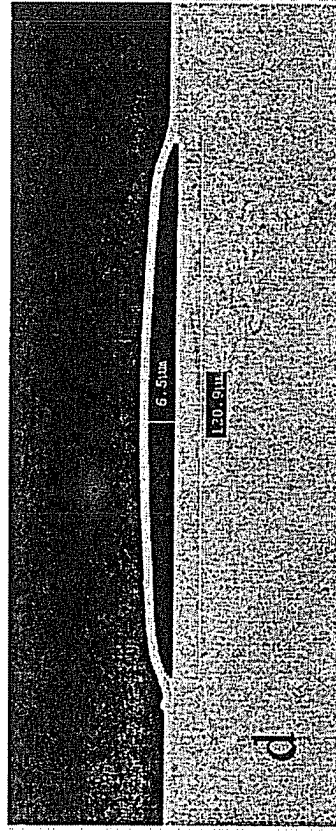
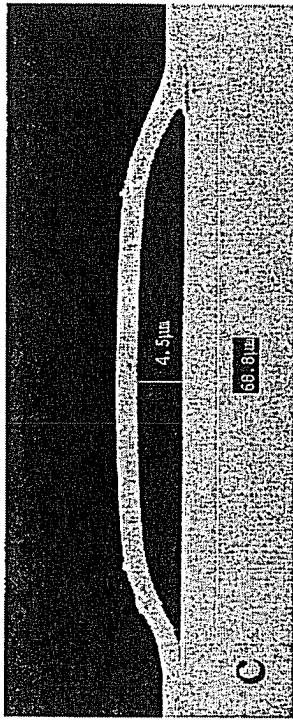


Figure 9

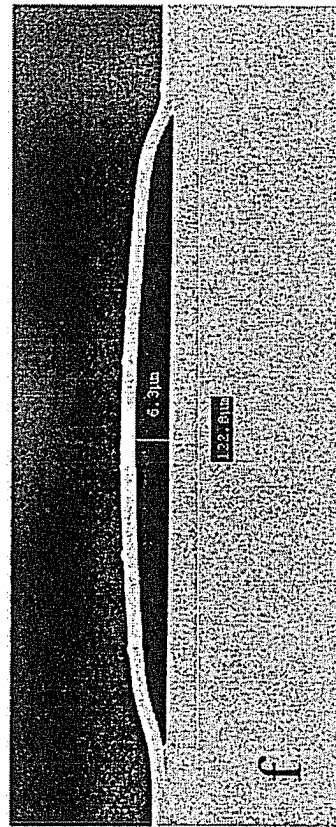
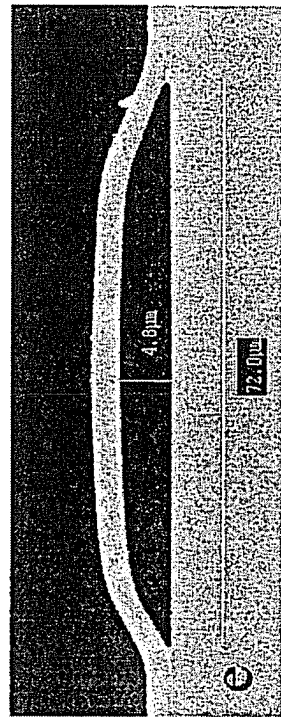


Figure 9

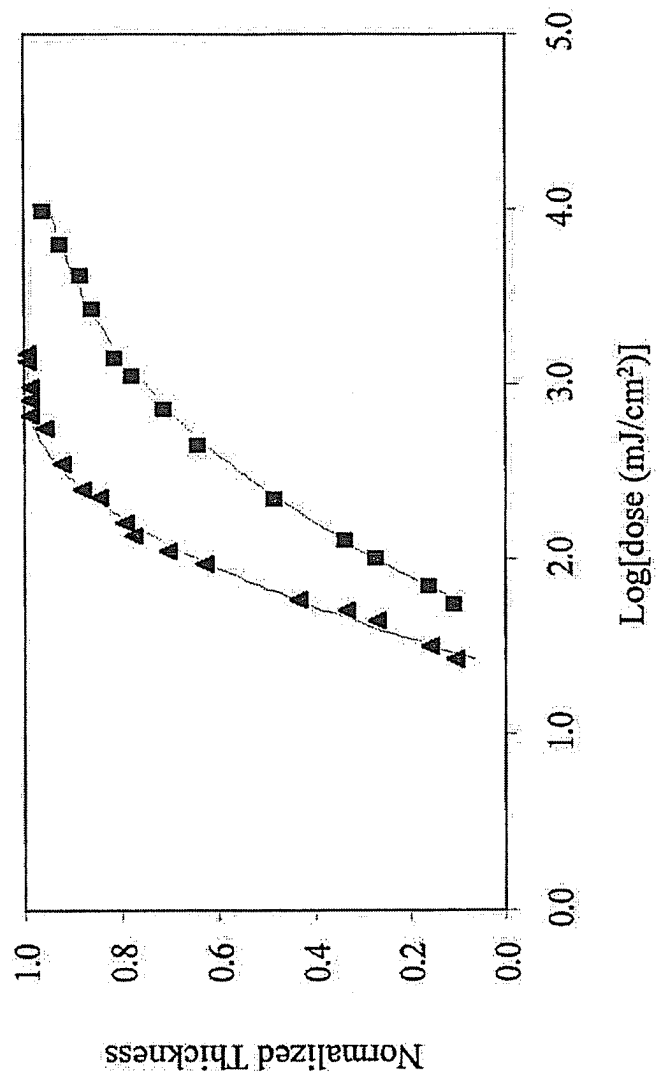


Figure 10

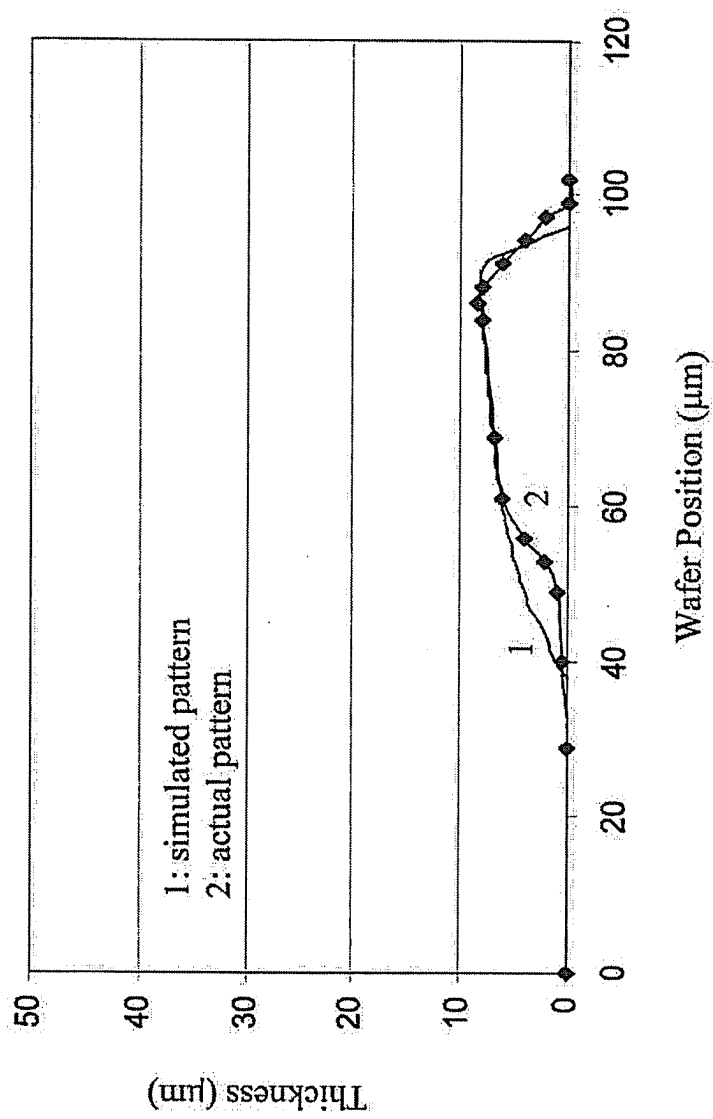


Figure 12

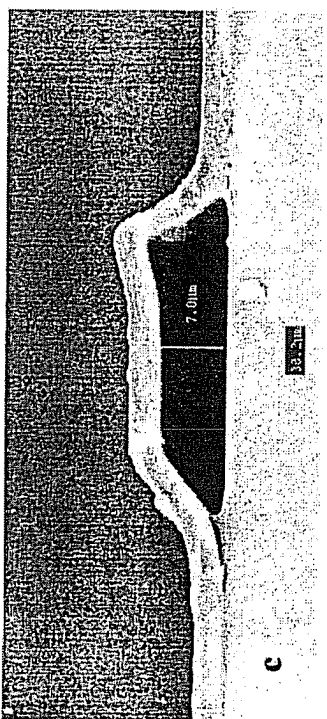
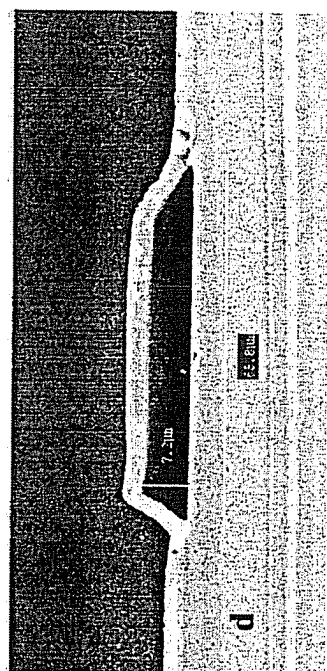
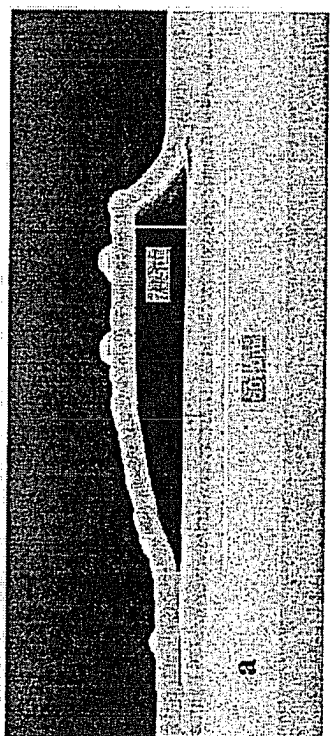
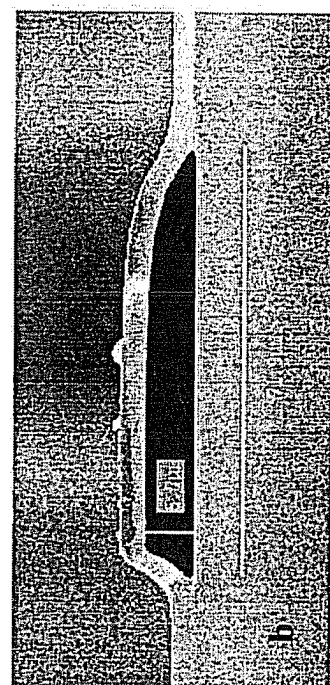


Figure 13

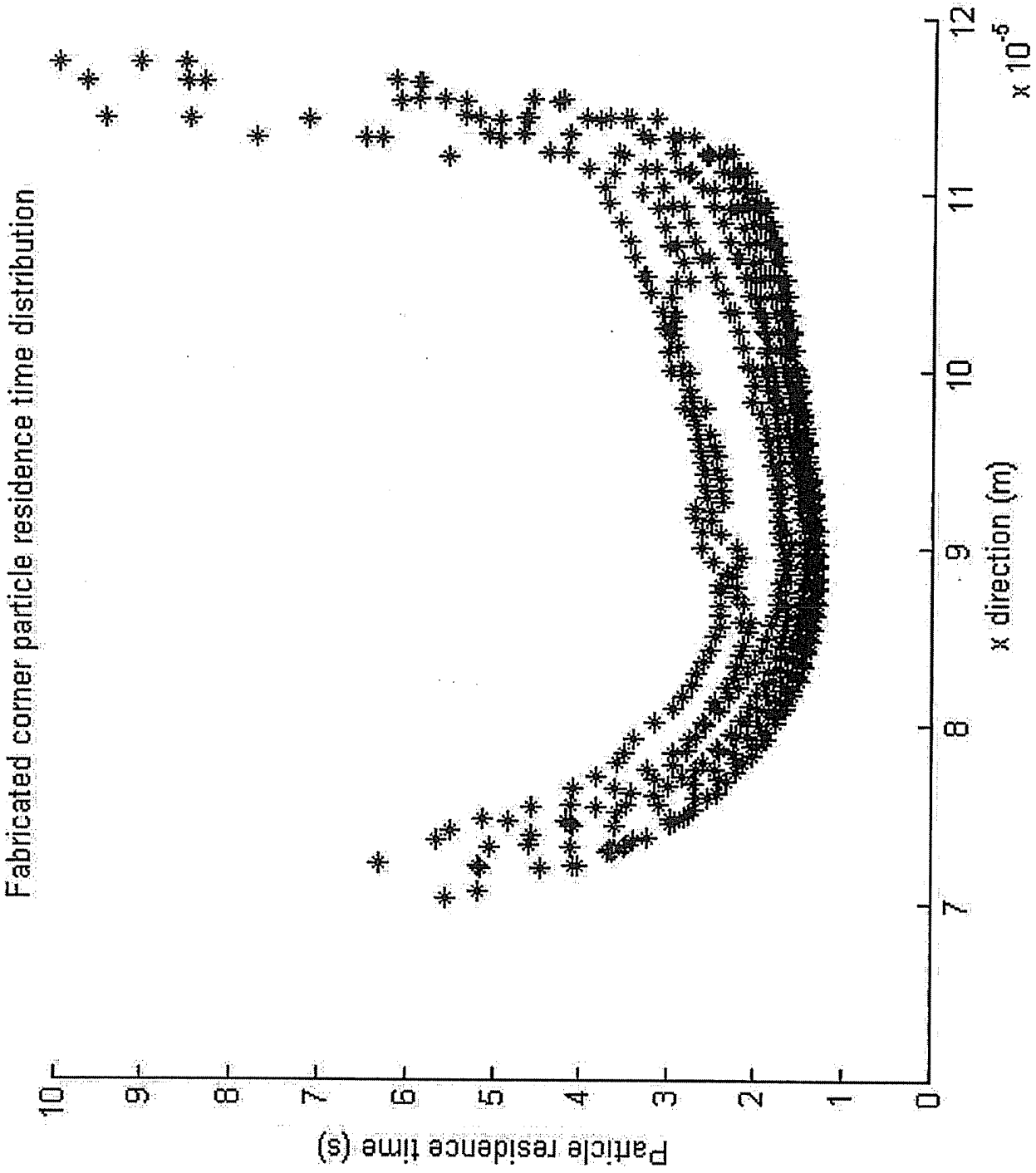


Figure 14

Microfluidic devices are becoming very important in several fields. The applications include rapid screening of drug synthesis, chemical synthesis, biological sensors, and microfuel cells, to name a few. In many applications, the devices involve flowing a fluid down a small channel. The applications often involve the analysis of a substance in the channel. A common problem occurs when the channel has a uniform height. For example, if a channel changes x/y direction (turns a corner), then the velocity of the fluid at the inner edge of the channel is greater than the furthest edge of the channel resulting in dispersion. At times, it would be desirable to have a region of the microfluidic device have a greater height so that a greater quantity of fluid will be present, such as for a chemical reactor.

A second improvement in this invention is the ability to use a photosensitive sacrificial polymer for the direct printing of microfluidic devices.

In this invention, we show that a photosensitive, sacrificial material is possible. We have demonstrated a negative tone, directly printable sacrificial polymer. The experiment below will serve as one example of how such a process may be carried out.

The sacrificial polymer is a co-polymer of 10 mole percent cyclohexyl acrylate norbornene and 90 mole percent butyl norbornene. The polymer was dissolved in mesitylene to a final composition of 16 weight percent. Also added to the solution was 4 weight percent benzyl ethyl ether (BEE). The BEE is known to generate free radicals when exposed to ultra violet light. The free radicals can cross link the norbornene copolymer. The norbornene copolymer with BEE was spin coated onto a silicon wafer at 2000 to 4000 RPM and then soft baked at 90 to 110°C. The thin film of norbornene with BEE was then exposed to ultraviolet light using a lithography mask (patterns of light and dark). The exposed regions cross linked due to the free radicals generated by the BEE. The cross linked region became less soluble in a solvent. The unexposed regions were dissolved away by using an appropriate solvent, like xylene or bioact. The remaining pattern was then encapsulated with a dielectric material, like polyimide or silicon dioxide. After encapsulating, the sacrificial polymer was thermally decomposed leaving a buried air-cavity. Figure 1, 2 and 3 show SEM cross sections of the channels. Thus, the direct photoprinting of a microfluidic device is demonstrated.

The second aspect of this invention is the three-dimensional nature of the channels. Show contrast curves for the photo printing process. That is, the higher the optical exposure, the more polymer is left. The thicker the polymer- the higher the microfluidic channel. The edges of the channels in Fig. 1, 2 and 3 show tapered profiles. With the contrast curves, channels of arbitrary shape can be made.

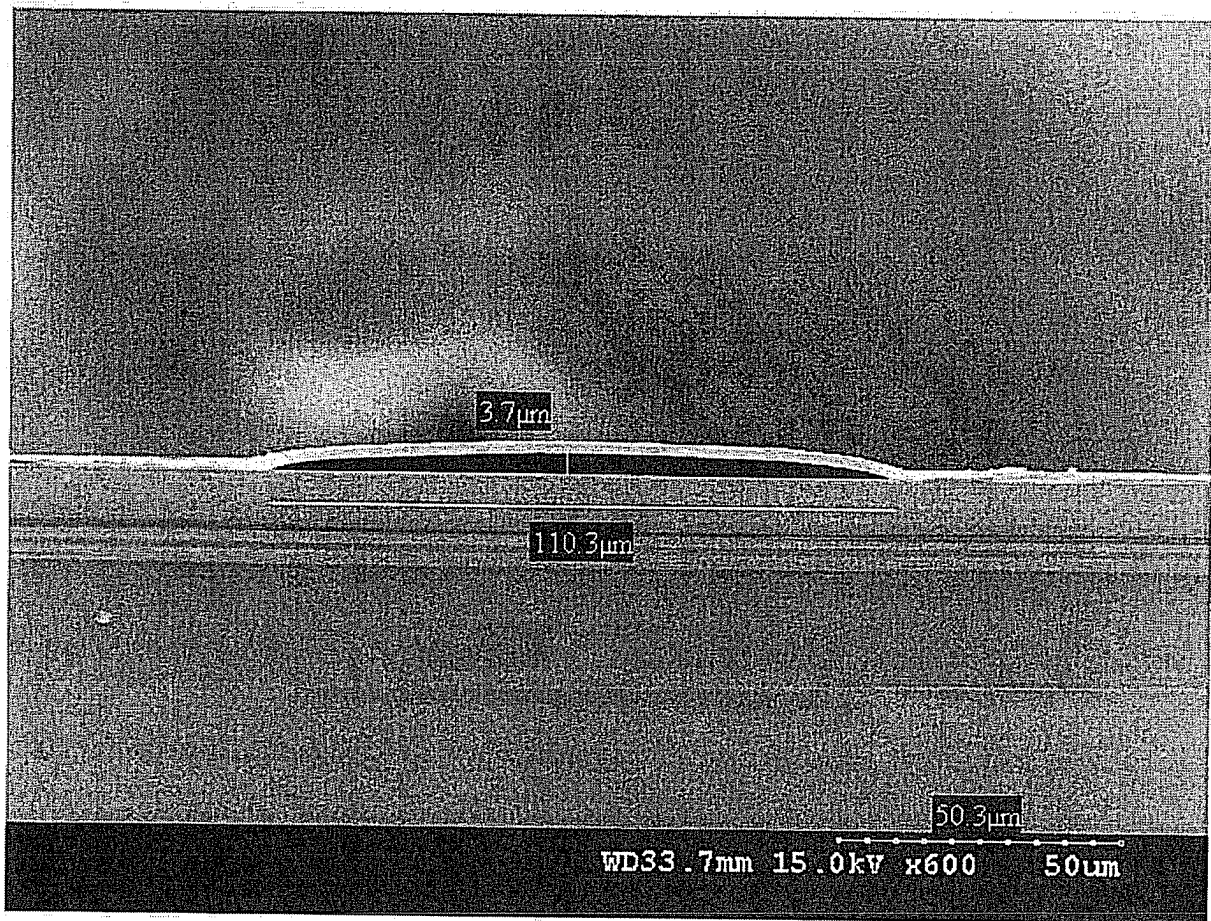


Fig. 1

GEORGIA TECH RESEARCH CORPORATION
PROPRIETARY INFORMATION

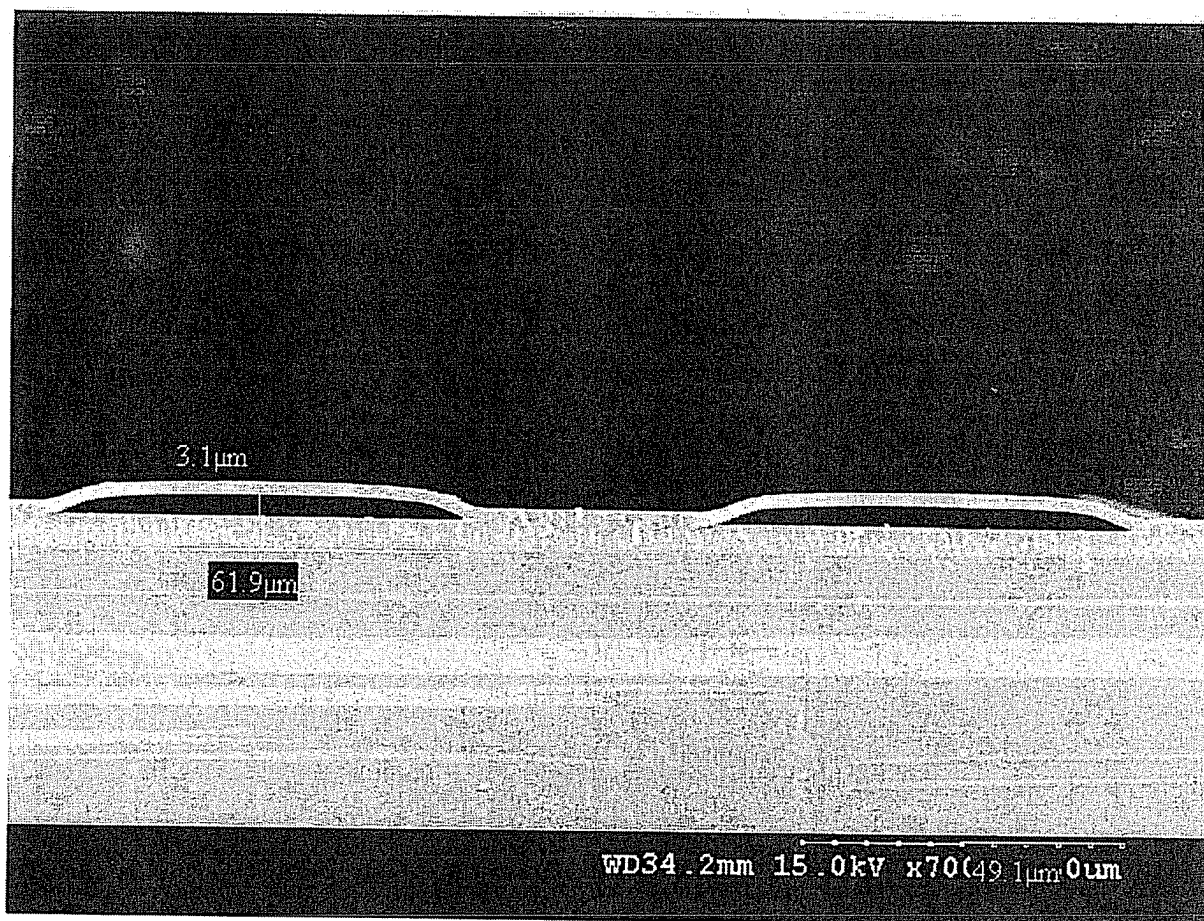


Fig. 2

GEORGIA TECH RESEARCH CORPORATION
PROPRIETARY INFORMATION

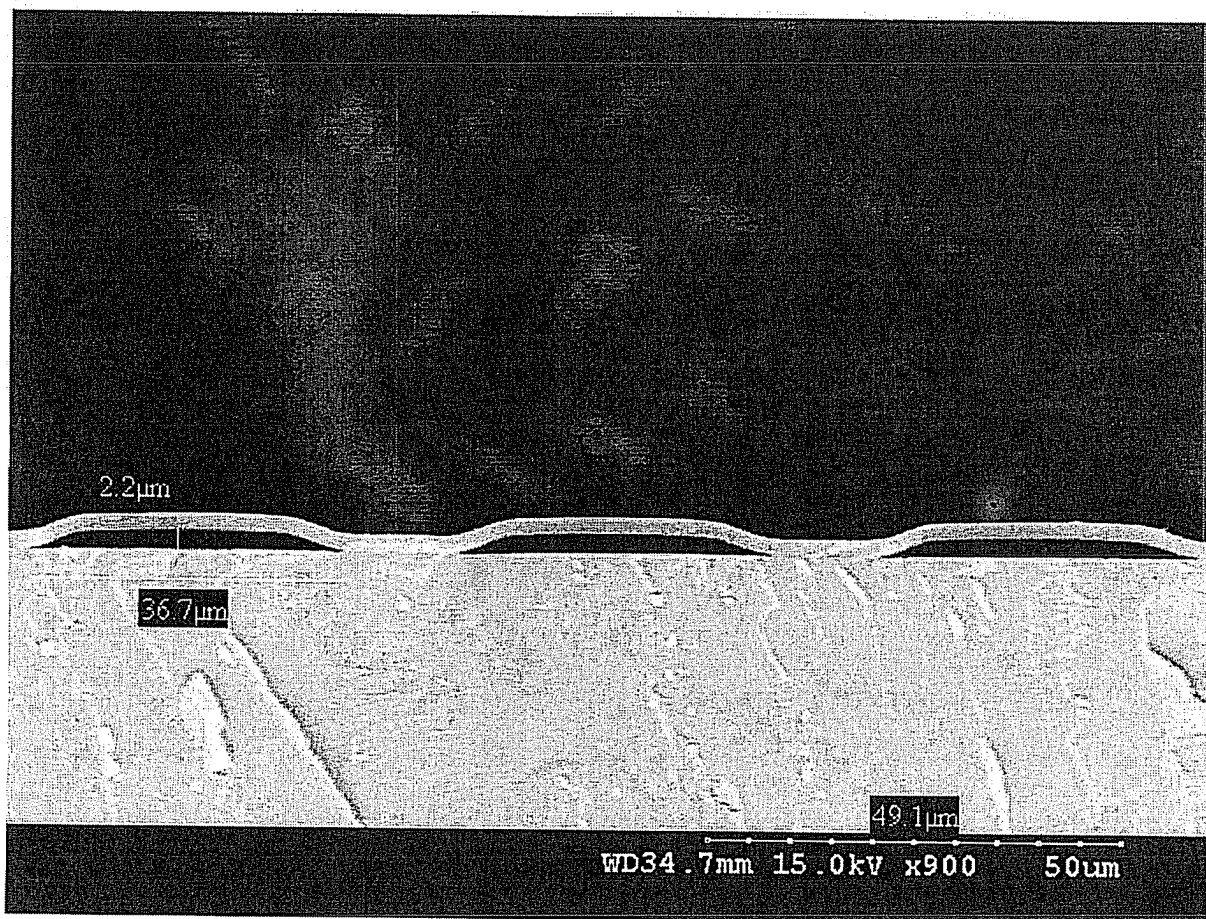


Fig - 3

GEORGIA TECH RESEARCH CORPORATION
PROPRIETARY INFORMATION

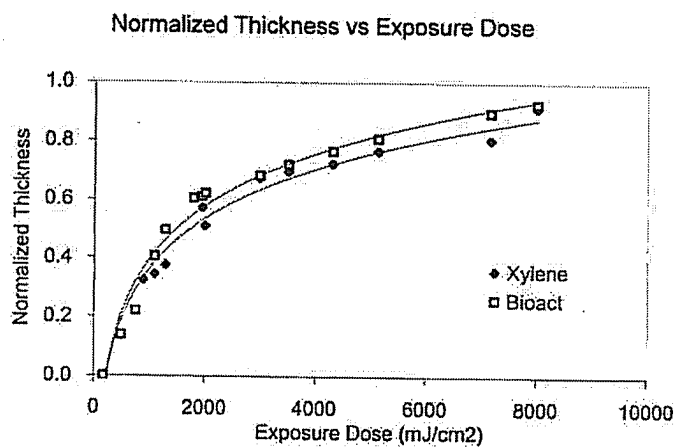
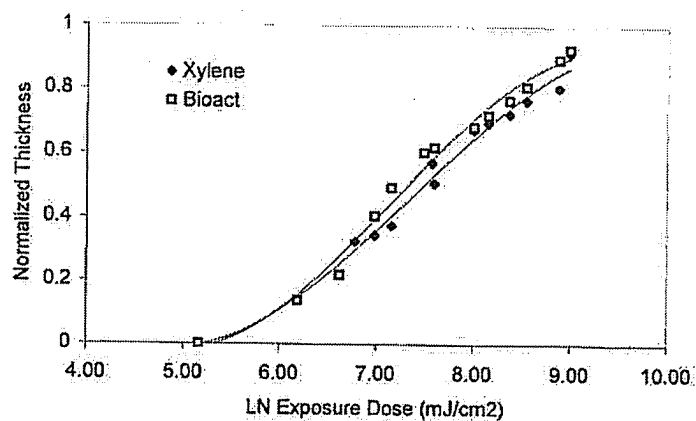


Fig. 4



Contrast Value: ~ 0.3

Fig. 5

GEORGIA TECH RESEARCH CORPORATION
PROPRIETARY INFORMATION

February 13, 2001

Dr. Paul Kohl
Chemical Engineering
Mail Code 0100

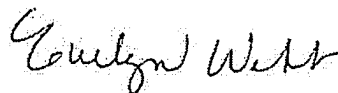
Dear Dr. Kohl:

We are writing to acknowledge receipt of the Invention Disclosure covering the invention entitled "Three-dimensional Microfluidic Device Fabrication". It is noted that your co-inventors are Sue Ann Bidstrup Allen, Clifford Lee Henderson and Xiaoqun Wu.

It is also noted that this invention was the result of sponsored research with NSF, GIT Project No. E-19-Y06.

For administrative purposes, we have assigned the identification number 2445 to the disclosure. Ms. Christi Kobatake, one of our Technology Licensing Associates, will be contacting you in the near future to discuss this invention disclosure with you.

Sincerely,



Evelyn Webb
Administrative Assistant

cc: Sue Ann Bidstrup Allen
Clifford Lee Henderson
Xiaoqun Wu
ID 2445

Georgia Institute of Technology
Atlanta, Georgia 30332-0415 U.S.A.
PHONE 404.894.6287 FAX 404.894.9728
<http://www.gtrc.gatech.edu>

A Unit of the University System of Georgia An Equal Education and Employment Opportunity Institution

- Ask Paul - an
improvement to
be in. to PFG?
Disclosed to them?
- if so, rel. contrib.?